Heterocycles in Organic Synthesis. Part 3.[1] Reversible Dearomatisation of Azoles: Formation of Triazabenzophenanthrenes [2]

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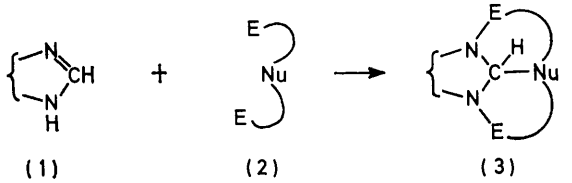
Benzimidazole undergoes reversible dearomatisation with 2,2'-iminodibenzoyl chloride to yield a triazahexacyclic compound (8a). Analogous cyclisations succeeded with 5,6-dimethylbenzimidazole and 4-quinazolone, and with acyclic amidines. Imidazole itself yields the diazocine derivative (19).

THE amidine group (1), itself highly stabilised by resonance, is a constituent of many heteroaromatic ring systems, *e.g.* imidazole. The aim of the present work was to cause the amidine group (1) to react with a multifunctional reagent containing two electrophilic terminal centres spaced from a central nucleophilic centre, to give derivatives of type (3). It was anticipated that such reactions would be reversible, and that it might be possible to carry out useful synthetic transformations on the dearomatised intermediate (3).



(1) (2) (3)

Preparation of Reagent.—In preliminary work with a number of compounds containing the grouping (2), results with 2,2'-iminodibenzoyl chloride (6) [3] were the most encouraging. This compound, which is stable at 20 °C without desiccation, was prepared in 88—94% yields from thionyl chloride and 2,2'-iminodibenzoic acid (5), itself made in 88% (rather than the quoted [4] 33%) yield by doubling the amount of copper catalyst used, and increasing the reaction time from 8 to 36 h. The acid chloride (6) was characterised as the corresponding dianilide,[3] dipiperidide,[3] and diphenyl ester.

Reaction with Benzimidazole.—The acid chloride (6) with benzimidazole gave the bis-amide (7). The carbonyl stretching absorption of this bis-amide showed two peaks at 1 700 and 1 670 cm^{-1}, probably as a result of hydrogen-bonding of some of the C=O with the NH group; *cf.* *N*-benzoylimidazole,[5] ν(C=O) 1 712 cm^{-1}. On pyrolysis of (7) at 180 °C and 1 mmHg 1 mol of benzimidazole sublimed off, to leave 4b,9a,13b-triazadibenz[*a*,*e*]acephenanthrylene-9,14-dione (8). The n.m.r. spectrum of (8) lacks a signal near δ 8.0 expected for H-2

[1] Part 2, J. B. Bapat, R. J. Blade, A. J. Boulton, J. Epsztajn, A. R. Katritzky, J. Lewis, P. Molina-Buendia, P.-L. Nie, and C. A. Ramsden, *Tetrahedron Letters*, 1976, 2691.

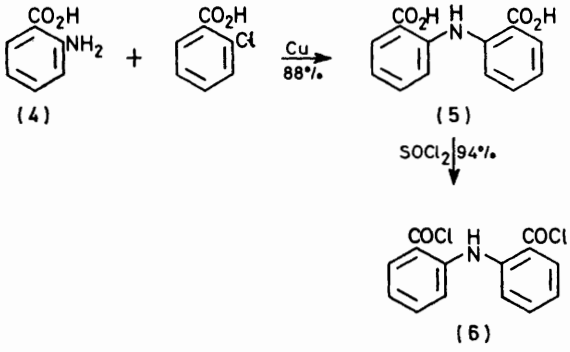
[2] Preliminary communication, J. C. Cass, A. R. Katritzky, R. L. Harlow, and S. H. Simonsen, *J.C.S. Chem., Comm.*, 1976, 48.

[3] E. Hannig and R. Brummer, *Pharmazie*, 1971, **26**, 135.

[4] N. S. Frumina and M. L. Nikurashina, *Metody Poluch. Khim. Reak. Prep.*, 1970, 63 (*Chem. Abs.*, 1972, **77**, 19,317).

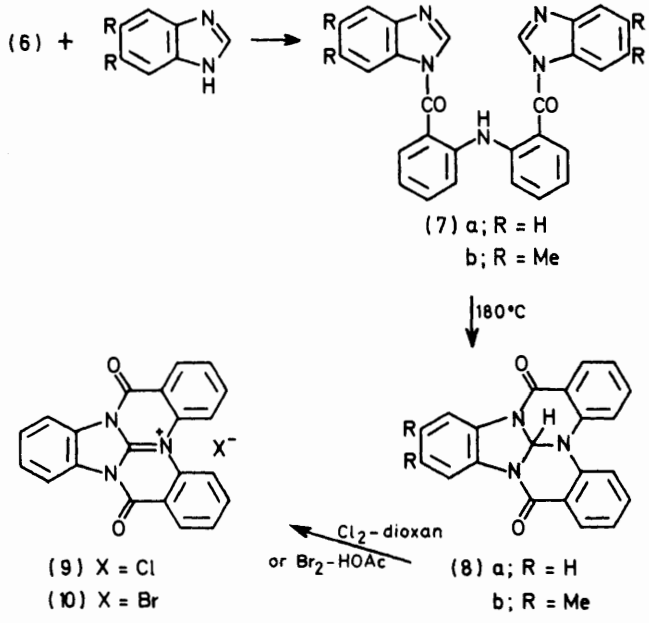
[5] H. A. Staab, W. Otting, and A. Ueberle, *Z. Elektrochem.*, 1957, **61**, 1000.

of a benzimidazole ring. Instead, a sharp singlet at δ 6.39 is observed for the proton of the central N_3CH group, well resolved from the twelve-proton aromatic peak. The ν(C=O) value (1 675 cm^{-1}) is typical of an amide. The mass spectrum of (8) is dominated by an intense ($M - 1$) peak (*m/e* 338), which is rationalised by the loss of the central hydrogen atom to give a resonance-stabilised



SCHEME 1

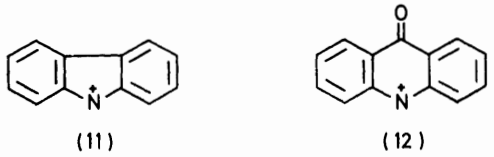
cation [*cf.* (9)]. The molecular ion abundance is 45% and the other fragment ions (all <10%) include (11) (9.6%) and (12) (6.2%). Structure (8) was finally confirmed by *X*-ray analysis.[2,6]



SCHEME 2

The hexacyclic derivative (8) was hydrolysed back to benzimidazole (63%) and iminodibenzoic acid by refluxing with 50% NaOH–H_2O for 8 h, although it was resistant to heating under reflux with 6M-HCl for 24 h.

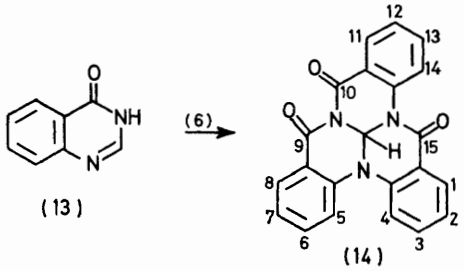
The hexacycle (8) was converted into the guanidinium salts (9) and (10) by action of halogens. The n.m.r. spectra of these lack any signal for a methine proton; they show merely an aromatic multiplet, which, centred at δ 7.9, is shifted significantly from that for the lactam (8), centred at δ *ca.* 7.1. The carbonyl absorption of (9)

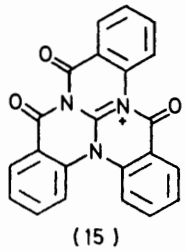


and (10) occurred at 1 730 cm^{-1}, showing a significant high frequency shift from the 1 675 cm^{-1} for the lactam (8).

Reaction Sequences Similar to that for Benzimidazole.—5,6-Dimethylbenzimidazole with the bis-chloride (6) gave a bis-amide (7b), which also underwent cyclisation, to (8b), at 170—180 °C and 1 mmHg with loss of one molecule of 5,6-dimethylbenzimidazole. The n.m.r. (singlet at δ 6.25) and i.r. [ν(C=O) 1 670 cm^{-1}] spectra for (8b) were similar to those for (8a).

4-Quinazolone (13) reacted with the acid chloride (6) to give the cyclisation product 4b,9a,14b-triazatribenzo-[*b,e,j*]phenalene-9,10,15-trione (14) directly; the bis-amide could not be isolated even in the presence of an excess of (13). The central methine proton signal at δ 6.88 and the intense (72%) $M - 1$ peak (*m/e* 366) (15) are characteristic of structure (14). The mass spectrum also shows a prominent parent peak (100%); loss of HCO and HCO_2 gives peaks at *m/e* 338 (7.4%) and 322 (72%). A peak at *m/e* 146 (15%) is ascribed to quinazolone, and the fragments left by loss of quinazolonyl and quinazolone occur at *m/e* 222 (11%) and 221 (35%). The *m/e* 222 fragment successively loses CO, CO, and C_2H_2 to give peaks at *m/e* 194 (41%) (12), 166 (40%) (11), and 140 (24%). The M^{2+} peak is visible at 183.5 (8.7%). The i.r. spectrum showed ν(C=O) bands at 1 745, 1 738, and 1 686 cm^{-1}.

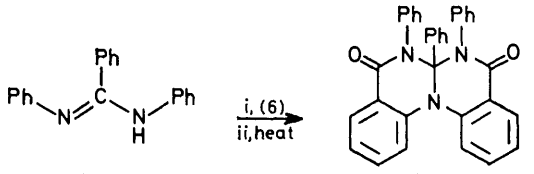




Reaction of Acyclic Amidines with the Acid Chloride (6).—*NN'*-Diphenylbenzamidine (16) gave the corresponding bis-amide which showed the expected spectral properties

[6] R. L. Harlow and S. H. Simonsen, *Acta Cryst.*, 1976, **32B**, 1606.

[ν(N–H) 3 370, ν(C=O) 1 658, and ν(C=N) 1 626 cm^{-1}]. At 170 °C and 1 mmHg, 0.96 mol of diphenylbenzamide sublimed leaving the tetracyclic product (17), ν(C=O) 1 665 cm^{-1} [no ν(C=N)].

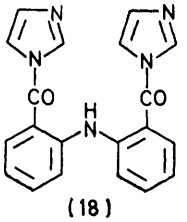


(16) (17)

Reaction with Imidazole.—Imidazole formed the expected bis-amide (18) as a viscous oil (which was easily hydrolysed by atmospheric moisture), converted on prolonged evacuation at 1 mmHg to a glass of ill-defined m.p. The ν(C=O) band at 1 680 cm^{-1} and the n.m.r. spectrum (especially 2 H singlet for ring H-2 at δ 8.0) confirm the structure. Boiling 2N-hydrochloric acid reconverted the amide (18) into iminodibenzoic acid (5); warming (18) with aniline yielded the corresponding bis-anilide.

At 150 °C and 1 mmHg, 1 mol of imidazole sublimed from the bis-amide (18) leaving 5,11-bis-[2-(imidazol-1-ylcarbonyl)phenyl]dibenzo[*b*,*f*][1,5]diazocine-6,12-dione (19). This showed ν(C=O) absorption at 1 715 cm^{-1} for the aroylimidazole CON [*cf.* *N*-benzoylimidazole,[5] ν(C=O) 1 712 cm^{-1}] and at 1 660 cm^{-1} for the diazocinedione C=O [*cf.* the parent dilactam (22),[7] ν(C=O) at 1 660 cm^{-1}] and still possessed the 2 H singlet at δ 8.1 for H-2 of the imidazole ring.

Hydrolysis of (19) with aqueous 6M-hydrochloric acid gave the dicarboxylic acid (20) [ν(C=O) 1 710 cm^{-1}]. The acid (20) was converted into the methyl ester (21) by diazomethane. The ester (21) exhibited a molecular-ion peak at *m*/*e* 506, and showed ν(C=O) bands at 1 720 (for CO_2Me) and 1 665 cm^{-1} (for CON). The n.m.r. signals of only two of the aromatic protons *ortho* to the carbonyl groups in (21) lie in the low-field region δ 7.80—8.10,



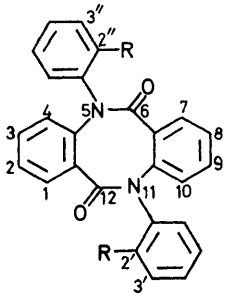
(18)

instead of the expected four. Evidently H-1 and -7 of the dibenzodiazocine ring are shielded by the amide carbonyls.

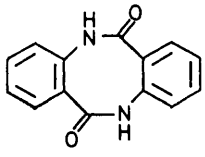
Attempts to trap the enediamine (23) from the pyrolysis of the imidazole bis-amide (18) with tetraphenylcyclopentadienone, phenyl isocyanate, and phthalic anhydride all failed.

Other Reactions.—Attempts to obtain the other cyclised products from heterocyclic bis-amides of 2,2′-iminodibenzoic acid (5) failed. The 4,5-diphenylimidazolyl derivative lost 1 mol of diphenylimidazole at 180 °C, but a tetrahydrofuran extract of the black residue contained several components (by t.l.c.). The pyrazole derivative sublimed unchanged at 210 °C. The corresponding bis-amides of indole and pyrrole could not be prepared.

General Conclusions.—It is striking that while reactions of the desired dearomatisation type succeeded for the bicyclic and also the acyclic series, the pyrolysis of the monocyclic derivatives of imidazole took a different course. The explanation must lie in the differing amounts of resonance energy lost in such cyclisations. In benzimidazole this is the difference between the aromaticity of the original ring system and that of benzene, while in the acyclic amidines it is simply the amine resonance energy. Both these quantities are felt intuitively to be



(19) R = CO–N
(20) R = CO_2H
(21) R = CO_2Me



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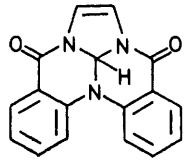

(23)

smaller than the complete loss of aromatic resonance energy for the monocyclic compounds. Unfortunately no experimental values are available and calculated resonance energies for imidazole (12.2—32.1 kcal mol^{-1}) and benzimidazole (48.7—68.8) vary widely.[8] This precludes a quantitative treatment at present.

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 237 and 257 spectrometers, u.v. spectra on a Pye–Unicam SP 800 spectrometer, ^{1}H n.m.r. spectra on Perkin-Elmer R-12 (60 MHz) and Varian HA-100 (100 MHz) instruments, and mass spectra with a Hitachi–Perkin-Elmer RMU-6E spectrometer. Analytical samples were routinely dried over P_2O_5 at 2 mmHg for 12 h. M.p.s were determined on a Kofler hot-stage apparatus.

2,2′-*Iminodibenzoic Acid* (5) (cf. *ref.* 3).—Anthranilic acid (45.5 g, 0.33 mol), 2-chlorobenzoic acid (47 g, 0.3 mol), K_2CO_3 (79 g, 0.5 mol), and Cu powder (5 g) were heated under reflux in pentyl alcohol (1 l) for 36 h. The mixture was filtered, and the filtrate extracted with water (3 × 200 ml). The residue in water (300 ml) was combined with the aqueous extract and boiled with activated charcoal (2 × 10 g). Acidification (pH 1) with 12M-HCl gave the acid (5) (65.5 g, 88%), which when washed with EtOH (3 × 100 ml) and dried at 100 °C at 1 mmHg, had m.p. 314—316 °C (from

[7] M. Kurihara, *Makromol. Chem.*, 1967, **105**, 84.
[8] H. Zimmermann and H. Geisenfelder, *Z. Elektrochem.*, 1961, **65**, 368.

EtOH) (lit.,[3] 295 °C) (Found: C, 65.2; H, 4.5; N, 5.2. Calc. for $C_{14}H_{11}NO_4$: C, 65.4; H, 4.3; N, 5.4%); *m/e* 257 (M^+).

2,2'-Iminodibenzoyl Chloride (6).—The acid (5) (15 g, 0.058 mol) was heated under reflux for 2 h with freshly distilled $SOCl_2$ (50 ml). The mixture was concentrated to 20 ml and poured at 0 °C into anhydrous light petroleum (b.p. 40—60 °C) (150 ml) to give a precipitate of the acid chloride (6). This was boiled with further light petroleum (100 ml); the mixture was cooled to 0 °C and refiltered, and the solid was washed with a third portion of ice-cold light petroleum (100 ml). Compound (6) was thus obtained as yellow prisms, m.p. 161—163 °C (lit.,[3] 155 °C) (16.2 g, 94%) (Found: C, 56.6; H, 3.2; Cl, 24.1; N, 4.8. Calc. for $C_{14}H_9Cl_2NO_2$: C, 57.2; H, 3.1; Cl, 24.1; N, 4.8%).

The dianilide, m.p. 196—199 °C (lit.,[3] 197 °C), and dipiperidide, m.p. 160—161 °C (lit.,[3] 162—163 °C), were prepared by literature methods.[3]

Diphenyl 2,2'-Iminodibenzoate.—The acid chloride (6) (0.294 g, 0.001 mol) was warmed with phenol (1 g) for 1 h at 100 °C; the product was dissolved in $CHCl_3$ (20 ml) and extracted with water (2 × 30 ml). Evaporation of the $CHCl_3$ gave the *ester* (0.15 g, 37%) as yellow prisms (from EtOH), m.p. 129—131 °C (Found: C, 76.1; H, 4.5; N, 3.7. $C_{26}H_{19}NO_4$ requires C, 76.3; H, 4.7; N, 3.4%); $\nu_{max.}$ (Nujol) 3 340 (–NH–) and 1 710 cm^{-1} (C=O).

1,1'-(2,2'-Iminodibenzoyl)bisbenzimidazole (7a).—The acid chloride (6) (2.94 g, 0.01 mol), benzimidazole (2.36 g, 0.02 mol), and Et_3N (2.02 g, 0.02 mol) were mixed and kept for 20 h at 20 °C in $[CH_2]_4O$ (100 ml). Precipitated Et_3N,HCl was removed and the filtrate concentrated. The *bis-amide* (7a) (3.5 g, 43%) crystallised from $[CH_2]_4O$ as pale yellow needles, m.p. 207—208 °C (Found: C, 73.1; H, 4.4; N, 15.2. $C_{28}H_{19}N_5O_2$ requires C, 73.5; H, 4.2; N, 15.3%); $\nu_{max.}$ (Nujol) 3 350 (NH), 1 700 and 1 670 (C=O), and 1 605 cm^{-1} (C=C); δ($CDCl_3$) 8.07 (2 H, s) and 6.95—8.10 (16 H, m); *m/e* 457 (M^+, 1%), 374 (3), 340 (12), 339 (52), 338 (100), 310 (3), 222 (3), 196 (18), 194 (9), 169 (10), 166 (20), 140 (9), 139 (8), 119 (12), 118 (55), 91 (32), 90 (16), 64 (17), 63 (21), 52 (6), 51 (4), and 50 (5).

4b,9a,13b-Triazadibenz[a,e]acephenanthrylene-9,14-dione (8a).—Compound (7a) (3.45 g, 7.5 × 10^{-3} mol) was heated in a sublimation apparatus at 180 °C and 1 mmHg for 6 h to give benzimidazole (0.97 g, 92%), m.p. 169—170 °C (lit.,[9] 170—172 °C) identical (i.r.) with an authentic specimen. The residue was extracted with $[CH_2]_4O$ to give on concentration the *dione* (8a), which crystallised from $[CH_2]_4O$ as pale yellow needles, m.p. 280—281 °C (1.87 g, 74%) (Found: C, 73.9; H, 4.1; N, 12.3. $C_{21}H_{13}N_3O_2$ requires C, 74.3; H, 3.9; N, 12.4%); $\nu_{max.}$ (Nujol) 1 675 (C=O) and 1 598 cm^{-1}; δ($CF_3{\cdot}CO_2H$) 6.60—7.60 (12 H, m) and 6.39 (1 H, s); *m/e* 339 (45%, M^+), 338 (100), 310 (3.2), 281 (2.2), 194 (6.2), 169 (8.6), 166 (9.6), 140 (6.2), 139 (4.3), 90 (3.4), 76 (4.4), 63 (2.4), 50 (2.3), and 39 (2.0).

Hydrolysis of the Hexacyclic Compound (8a).—Compound (8a) (0.10 g, 2.96 × 10^{-4} mol) was heated under reflux with 50% NaOH–H_2O (10 ml) for 8 h; the mixture was then diluted with water (25 ml) and extracted with ether (5 × 40 ml). Evaporation of the extracts afforded benzimidazole (0.022 g, 63%), which crystallised from water as fine needles, m.p. 168—169 °C (lit.,[9] 170—172 °C).

Acidification of the aqueous solution with HCl gave a brown precipitate which was dissolved in aqueous 5% $NaHCO_3$ and was reprecipitated with HCl to give 2,2'-iminodibenzoic acid (0.043 g, 57%), m.p. 298—300 °C (lit.,[3] 295 °C), identical (i.r.) with an authentic sample.

9,14-Dioxo-4b,9a,13b-triazadibenz[a,e]acephenanthrylium Bromide (10).—Bromine (1.6 g, 0.01 mol) in glacial acetic acid (50 ml) was added dropwise to (8a) (1.7 g, 0.005 mol) in refluxing acetic acid (50 ml) during 15 min. After 10 min more under reflux, the mixture was allowed to cool to give the *bromide* (10) (2.09 g, 100%), which crystallised from HOAc–$CF_3{\cdot}CO_2H$ (1 : 3) as needles, m.p. >360 °C (Found: C, 60.2; H, 3.0; Br, 19.1; N, 10.1. $C_{21}H_{12}BrN_5O_2$ requires C, 60.3; H, 2.9; Br, 19.1; N, 10.0%); $\nu_{max.}$ (Nujol) 1 730 cm^{-1} (C=O); δ($CF_3{\cdot}CO_2H$) 7.30—8.50 (all protons, m).

9,14-Dioxo-4b,9a,13b-triazadibenz[a,e]acephenanthrylium Chloride (9).—A slow stream of dry chlorine was passed through a solution of the hexacyclic compound (8a) (2.0 g, 0.006 mol) in refluxing dioxan (100 ml) for 1 min. The precipitate was removed and the filtrate treated with further chlorine until precipitation was complete. The combined precipitates were crystallised from glacial acetic acid to give the *chloride* (9) as needles (2.0 g, 90%), m.p. 296 °C (decomp.) (Found: C, 67.0; H, 3.3; Cl, 9.6; N, 11.1. $C_{21}H_{12}ClN_3O_2$ requires C, 67.4; H, 3.2; Cl, 9.5; N, 11.2%), $\nu_{max.}$ (Nujol) 1 730 cm^{-1} (C=O).

5,5',6,6'-Tetramethyl-1,1'-(2,2'-iminodibenzoyl)bisbenzimidazole (7b).—A procedure similar to that for (7a) gave the *dimethyl bis-amide* (68%) as pale yellow needles, m.p. 206—207 °C (from $[CH_2]_4O$) (Found: C, 74.9; H, 5.2; N, 13.6. $C_{32}H_{27}N_5O_2$ requires C, 74.8; H, 5.3; N, 13.6%); $\nu_{max.}$ (Nujol) 3 310 (NH), 1 690 and 1 670 (C=O), and 1 580 cm^{-1}.

11,12-Dimethyl-4b,9a,13b-triazadibenz[a,e]acephenanthrylene-9,14-dione (8b).—Heating (7b) by the procedure for (7a) gave a sublimate of 5,6-dimethylbenzimidazole, m.p. 204—206 °C (100 mole %) (lit.,[10] 205—206 °C), identical (i.r.) with an authentic specimen, and a residue of the *dione* (8b) (60%), which formed pale yellow needles, m.p. 262—264 °C (from dioxan) (Found: C, 74.8; H, 4.9; N, 11.3. $C_{23}H_{17}N_3O_2$ requires C, 75.2; H, 4.7; N, 11.4%); $\nu_{max.}$ (Nujol) 1 670 (C=O) and 1 610 cm^{-1}; δ($CF_3{\cdot}CO_2H$) 6.60—7.60 (10 H, m), 6.25 (1 H, s), and 1.72 (6 H, s, 11- and 12-CH_3).

4b,9a,14b-Triazatribenzo[b,e,j]phenalene-9,10,15-trione (14).—The acid chloride (6) (2.94 g, 0.01 mol), 4-quinazolone[11] (13) (1.46 g, 0.01 mol), and Et_3N (3.03 g, 0.03 mol) in $[CH_2]_4O$ (150 ml) were heated under reflux for 4 h. The mixture was filtered and the filtrate was concentrated to 30 ml and diluted with benzene (50 ml) to yield the *trione* (14) (2.0 g, 55%), which gave pale yellow needles, m.p. 314—316 °C (from Me_2CO–$CHCl_3$) (Found: C, 71.8; H, 3.3; N, 11.5. $C_{22}H_{13}N_3O_3$ requires C, 71.9; H, 3.6; N, 11.4%); $\nu_{max.}$ (Nujol) 1 745, 1 738, and 1 686 (C=O), 1 612, and 1 602 cm^{-1} (C=C); δ($CDCl_3$) 6.88 [1 H, s, (>N)$_3$CH] and 6.49—8.03 (12 H, m); *m/e* 367 (100%, M^+), 366 (72), 338 (7.4, M – CHO), 322 (72), 222 (11), 221 (35), 195 (13), 194 (41), 183.5 (8.7, M^{2+}), 167 (7.4), 166 (40), 146 (15), 140 (24), 139 (12), 129 (32), 90 (19), 76 (11), and 65 (6.7).

NN'N''N'''-Tetraphenyl-NN''-(2,2'-iminodibenzoyl)dibenzamidine.—The acid chloride (6) (2.94 g, 0.01 mol), *NN'*-diphenylbenzamidine (5.44 g, 0.02 mol), and Et_3N (3.03 g, 0.03 mol) in $[CH_2]_4O$ (100 ml) were kept for 20 h at 20 °C. The mixture was filtered and evaporated (30 °C at 20 mmHg) to give the *bis-amide* which crystallised from benzene–light

[9] E. C. Wagner and W. H. Millett, *Org. Synth.*, Coll. Vol. II, 1943, p. 65.

[10] 'Handbook of Chemistry and Physics,' 51st edn., ed. R. C. Weast, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970.

[11] S. v. Niementowski, *J. prakt. Chem.*, 1895, [2] **51**, 564 [*J. Chem. Soc. Abs.*, 1895, **68** (i), 571].

petroleum (b.p. 60—80 °C) (2 : 1) as yellow prisms (2.5 g, 33%), m.p. 155—160 °C (Found: C, 81.4; H, 5.1. $C_{52}H_{39}N_5O_2$ requires C, 81.5; H, 5.1%); δ($CDCl_3$) 8.08—8.45 (4 H, m), 7.75—8.08 (2 H, m), and 6.60—7.65 (32 H, m); $\nu_{max.}$ (Nujol) 3 370 (NH), 1 658 (C=O), 1 626 (C=N), 1 590, and 1 572 cm^{-1}.

The bis-amide (0.2 g) was heated at 170 °C and 1 mmHg for 8 h to give a sublimate of diphenylbenzamidine (0.066 g) (identified by i.r. spectrum). The residue crystallised from C_6H_6–$[CH_2]_4O$ as pale yellow needles of 6,6a,7-*triphenyl*-6,7,12b-*triazabenzo*[c]*phenanthrene*-5,8-*dione* (17) (0.095 g, 74%), m.p. 156—157 °C (Found: C, 81.1; H, 4.9; N, 9.1. $C_{33}H_{23}N_3O_2$ requires C, 80.3; H, 4.7; N, 8.5%); $\nu_{max.}$ (Nujol) 1 665, 1 650, and 1 590 cm^{-1}.

5,11-*Bis*-(2-*carboxyphenyl*)*dibenzo*[b,f][1,5]*diazocine*-6,12-*dione* (20).—2,2′-Iminodibenzoyl chloride (2.94 g, 0.01 mol), imidazole (1,38 g, 0.02 mol), and Et_3N (2.7 g, 0.026 mol) in $[CH_2]_4O$ (150 ml) were kept for 10 min at 20 °C. The mixture was filtered and the filtrate was evaporated at 20 °C (36 h at 1 mmHg) to give crude 1,1′-(2,2′-iminodibenzoyl)diimidazole (18) as a yellow glass, m.p. 50—60 °C, $\nu_{max.}$ (Nujol) 1 715—1 650br (C=O) and 1 570 cm^{-1}; δ($CDCl_3$) 8.0 (2 H, s), 7.4—7.8 (8 H), and 6.9—7.3 (4 H).

This diphenylamine (18) (5.0 g, 0.014 mol) was heated in a sublimation apparatus at 150 °C for 8 h. The sublimed imidazole (0.95 g, 100 mole %), m.p. 86 °C (lit.,[10] 90—91 °C) identical (i.r.) with an authentic specimen, was removed, and the residue dissolved in $[CH_2]_4O$ (30 ml) and reprecipitated by anhydrous ether (150 ml) to give the crude imidazolyldiazocine (19) (2.0 g, 50%), m.p. 263—265 °C, $\nu_{max.}$ (Nujol) 1 715, 1 660 (C=O), and 1 600 cm^{-1}; δ[$CDCl_3$–$(CD_3)_2SO$] 8.1 (2 H, m) and 7.0—8.0 (20 H, m).

The amide (19) (3.49 g) was heated under reflux with HCl (100 ml, 50% v/v) for 24 h. The precipitate was washed with water (2 × 50 ml) and recrystallised from propan-2-ol to give the 5,11-*bis*-(2-*carboxyphenyl*)*dibenzo*[b,f][1,5]*diazocine*-6,12-*dione* (20) as pale yellow microcrystals (2.35 g, 81%), m.p. 280—290 °C (Found: N, 5.5. $C_{28}H_{18}N_2O_6$ requires N, 5.8%); $\nu_{max.}$ (Nujol) 3 360br (O–H), 1 710 and 1 640 (C=O), and 1 600 cm^{-1}.

5,11-*Bis*-(2-*methoxycarbonylphenyl*)*dibenzo*[b,f][1,5]*diazocine*-6,12-*dione* (21).—The dicarboxylic acid (20) (1.67 g) was stirred with diazomethane in ether (50 ml; 0.36 M) for 1 h at 20 °C. The excess of diazomethane was destroyed by dropwise addition of glacial acetic acid (2 ml) and the solution was filtered. The filtrate was evaporated to dryness to give the *dimethyl ester* (21), which formed yellow prisms (1.1 g, 63%), m.p. 264—266 °C (from EtOH) (Found: N, 5.6. $C_{30}H_{22}N_2O_6$ requires N, 5.5%); $\nu_{max.}$ (Nujol) 1 720 and 1 665 (C=O) and 1 600 cm^{-1}; δ ($CDCl_3$) 7.8—8.1 (2 H, m, H-3′ and -3″), 7.1—7.6 (14 H), and 4.05 (6 H, s, Me); *m/e* 506.147 6 (100%) (M^+) ($^{12}C_{30}{}^1H_{22}{}^{14}N_2{}^{16}O_6$ requires 506.147 75).

4,4′,5,5′-*Tetraphenyl*-1,1′-(2,2′-*iminodibenzoyl*)*di-imidazole*.—This was prepared from (6) in 62% yield by the procedure for (7a) and (7b) and crystallised from toluene as yellow *prisms*, m.p. 207—210 °C (Found: C, 79.2; H, 5.2; N, 9.9. $C_{44}H_{31}N_5O_2$ requires C, 79.9; H, 4.7; N, 10.6%); $\nu_{max.}$ (Nujol) 3 370 (NH), 1 680 (C=O), 1 600, 1 580, and 1 500 cm^{-1} (C=C).

1,1′-(2,2′-*Iminodibenzoyl*)*dipyrazole*.— 2,2′-Iminodibenzoyl chloride (6) (1.47 g, 0.005 mol), pyrazole (0.68 g, 0.01 mol), and Et_3N (2 g) in $[CH_2]_4O$ (75 ml) were kept for 1 h at 20 °C. The mixture was filtered and the filtrate concentrated to give the *pyrazolyl amide*, which formed yellow prisms (1.0 g, 58%), m.p. 185—187 °C (from $[CH_2]_4O$) (Found: C, 66.7; H, 4.2; N, 19.6. $C_{20}H_{15}N_5O_2$ requires C, 67.2; H, 4.2; N, 19.6%); $\nu_{max.}$ (Nujol) 3 370 (N–H), 1 700, 1 675 (C=O), 1 575, and 1 510 cm^{-1}; δ($CDCl_3$) 8.47 (2 H, d, *J* 6 Hz), 7.9—6.9 (10 H), and 6.49 (2 H, dd, *J* 6 and 3 Hz).

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