Photocyclization of N-(Dialkylaminoalkyl) Aromatic 1,2-Dicarboximides. *X*-Ray Molecular Structure of a Stereoisomer of 4-Benzyl-2-hydroxy-3-phenyl-4,6-diazatricyclo[6.4.0.0^{2,6}]dodeca-1(12),8,10-trien-7-one†

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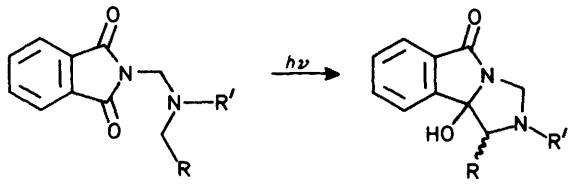
U.v. irradiation of Mannich bases derived from chloro- or methoxycarbonyl (but not nitro)-substituted phthalimides, pyridinedicarboximides, or naphthalene-2,3-dicarboximide gives rise to products with a new imidazolidine ring. Substrates from unsymmetrical imides lead preferentially (though not exclusively) to one orientation of reaction. Two diastereoisomeric products are often formed, and the relative stereochemistry can be assigned on the basis of n.m.r. data; in one case the stereochemistry is confirmed by *X*-ray crystallographic analysis. The two diastereoisomers are, under certain conditions, interconverted photochemically.

N-Substituted phthalimides can take part in a variety of photochemical reactions,[1,2] and photocyclization by way of hydrogen transfer to an oxygen atom of the excited imide group provides a useful route to certain heterocyclic systems. We have previously reported[3] that photocyclization of *N*-(dialkylaminomethyl)phthalimides [*e.g.* (**1**)—(**3**)] with a wide range of amine substituents gives imidazo[4,3-*a*]isoindole derivatives [*e.g.* (**4**)—(**6**)], and that the mechanism probably involves an (n,π^*) singlet excited state of the phthalimide.[4]

Analogous cyclized compounds in which the heterocyclic ring formed by cyclization is six- or seven-membered[5,6] or larger[7] are formed in similar reactions from imides with a longer carbon chain between the two nitrogen atoms. The situation with aliphatic imides is similar in that diaza- or triazabicyclic or -polycyclic products are formed, often in good yield, on irradiation of Mannich bases derived from succinimides,[8] glutarimides, or hydantoins,[9] but the formation of larger rings is generally inefficient except for derivatives of maleimides.[10] There are few reports of photocyclization reactions involving ring-substituted phthalimides or other aryl imides. *N*-(*o*-Tolyl)phthalimides with electron-withdrawing (Cl, CN, CO_2Me, $CONH_2$) groups in the phthalimide ring give approximately 1:1 mixtures of positional isomers of cyclized products on irradiation;[11] those with electron-donating (NH_2, NMe_2, OMe) groups in the ring resist reaction. Photoreaction of 4-substituted *N*-methylphthalimides with alkenes in methanol gives mixtures of positional isomers of adducts that incorporate solvent,[12] although in acetonitrile photoaddition products are obtained regioselectively.[13] These results are interpreted in terms of an initial electron-transfer mechanism.

We now report that photocyclization occurs for *N*-(dialkylaminomethyl)-substituted mono- and di-chlorophthalimides, 4-methoxycarbonylphthalimide, pyridine-2,3- and pyridine-3,4-dicarboximide, and naphthalene-2,3-dicarboximide. The results provide qualitative evidence in support of the proposed electron-transfer mechanism. Unsymmetrical imides give mixtures of regioisomeric photoproducts, and some of the products are obtained as mixtures of diastereoisomers. These isomers can be separated, and their stereochemistry is assigned on the basis of n.m.r. and *X*-ray data. In two cases a study of the photochemical interconversion of the stereoisomers gives results that can be correlated with their absorption properties.



(**1**) R = Ph, R′ = CH_2Ph (**4**)
(**2**) R = $CH{=}CH_2$, R′ = $CH_2CH{=}CH_2$ (**5**)
(**3**) RR′ = o-$C_6H_4CH_2CH_2$ (**6**)

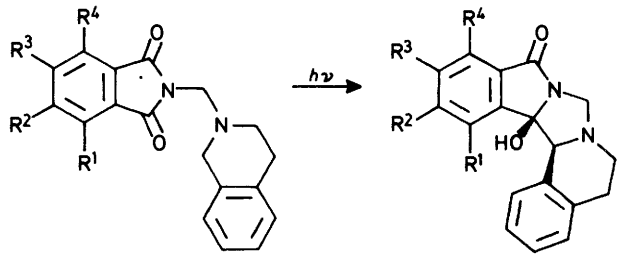
Results and Discussion

Like the analogous unsubstituted phthalimide (**3**),[3] the 4,5-dichlorophthalimide (**7**) undergoes ready photocyclization to give a good yield of pentacyclic product (**13**) with an imidazolidine ring. Elemental analysis shows that the product is an isomer of (**7**); the i.r. spectrum has a single C=O and an O–H stretching band; the ^{13}C n.m.r. spectrum shows a single carbonyl signal at δ_C 171.5 p.p.m. and a signal for a quaternary carbon at 97.2 p.p.m.; and the ^1H n.m.r. spectrum exhibits a characteristic AB pattern at δ_H 4.30 and 4.65, arising from the methylene group of the new ring.

The 3-chlorophthalimide (**8**) gives a mixture of products (**14**) and (**15**). The isomer that can be isolated in higher yield is assigned structure (**15**) on the basis of evidence from the ^1H n.m.r. spectra. In the aromatic proton region, the spectrum of (**14**) shows a signal near δ_H 7.5 corresponding to the position expected for a proton *ortho* to carbonyl as in the spectrum of compound (**8**); this signal is absent from the spectrum of (**15**). The signals for two of the methylene protons in the tetrahydroisoquinoline unit of (**14**) are at unusually low field (δ_H 3.4—3.8), but the cause of this effect is not known.

The 4-chlorophthalimide (**9**) also gives a mixture of positional isomers (**16**) and (**17**). High-field n.m.r. analysis of the total crude product (separated from residual starting material by column chromatography) indicates that there is an equal mixture (47:53) of the two compounds, but although there are clear differences in the aromatic region of the spectrum, the AB

† *Supplementary data available* (No. SUP 56102, 2 pp.): thermal parameters for non-hydrogen atoms for compound (**37**). See Instructions for Authors, 1985, Issue 1. Structure factors are available from the editorial office on request.



(7) $R^1 = R^4 = H$, $R^2 = R^3 = Cl$
(8) $R^1 = Cl$, $R^2 = R^3 = R^4 = H$
(9) $R^1 = R^3 = R^4 = H$, $R^2 = Cl$
(10) $R^1 = NO_2$, $R^2 = R^3 = R^4 = H$
(11) $R^1 = R^3 = R^4 = H$, $R^2 = NO_2$
(12) $R^1 = R^3 = R^4 = H$, $R^2 = CO_2Me$

(13) $R^1 = R^4 = H$, $R^2 = R^3 = Cl$
(14) $R^1 = Cl$, $R^2 = R^3 = R^4 = H$
(15) $R^1 = R^2 = R^3 = H$, $R^4 = Cl$
(16) $R^1 = R^3 = R^4 = H$, $R^2 = Cl$
(17) $R^1 = R^2 = R^4 = H$, $R^3 = Cl$
(18) $R^1 = R^3 = R^4 = H$, $R^2 = CO_2Me$
(19) $R^1 = R^2 = R^4 = H$, $R^3 = CO_2Me$

patterns for the NCH_2N unit, and the singlet for the bridgehead methine, are almost identical for (**16**) and (**17**). Recrystallization of the mixture afforded a pure sample of (**16**), but pure samples of (**17**) could not be obtained. The main evidence for the assignment of structure comes from the positions of the dd signals for the three aromatic protons of the chloro-substituted ring: for (**16**) these are at 6.98 (*J* 2 and 0.5 Hz, 4-H), 7.19 (*J* 8 and 2 Hz, 6-H), and 7.39 (*J* 8 and 0.5 Hz, 7-H), and for (**17**) at 6.91 (*J* 8 and 0.5 Hz, 4-H), 7.115 (*J* 8 and 2 Hz, 5-H), and 7.40 (*J* 2 and 0.5 Hz, 7-H). Clearly the chlorine has little effect on the chemical-shift values, but the pattern of *ortho* (8 Hz), *meta* (2 Hz), and *para* (0.5 Hz) coupling constants is unambiguous.

We were unsuccessful in our attempts at isolating products after irradiation of various Mannich bases of tetrachloro- or tetrabromo-phthalimide, although spectroscopic evidence suggested that cyclized products were formed. However, irradiation of the nitrophthalimides (**10**) and (**11**) leads to slow loss of substrate without the formation of products corresponding to those obtained in other photocyclizations. Small amounts of very insoluble materials were isolated, but their composition could not be elucidated fully because of their low solubility in n.m.r. solvents and their high m.p. I.r. evidence, supported by ^1H n.m.r. information, suggests that the imide group is still present in the product, and reaction has occurred at the nitro group.

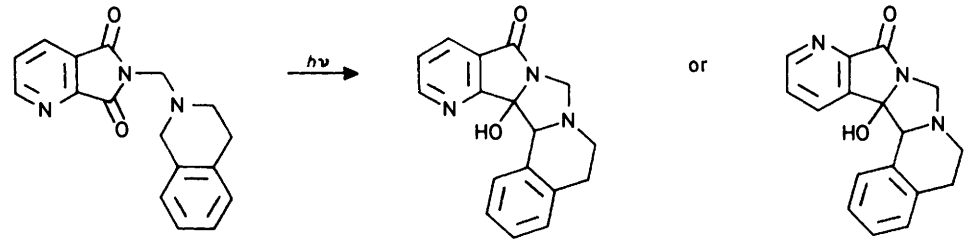
The 4-methoxycarbonyl compound (**12**) gives, in high yield, a mixture of photocyclized products (ratio *ca.* 2:1) which can be partially separated to yield samples whose major characteristics correspond to products (**18**) and (**19**). The isomer isolated in larger quantities is (**19**), as evidenced by a doublet (*J* 1.5 Hz) in the ^1H n.m.r. spectrum at δ_H 8.02, which we assign to the proton (7-H) *ortho* to the lactam carbonyl and *ortho* also to the methoxycarbonyl substituent. This isomer also shows a signal in the carbon n.m.r. spectrum at δ_C 152.4 p.p.m., corresponding to a quaternary carbon adjacent to C(OH) and *para* to the methoxycarbonyl group; the corresponding signal in the spectrum of (**18**) is at δ_C 148.2 p.p.m.

The lack of high regioselectivity in the photocyclization reactions of (**8**), (**9**), and (**12**) is in keeping with findings in the *N*-(*o*-tolyl)phthalimide series,[11] but it contrasts to a certain extent with the selectivity encountered in the photoreactions of *N*-methylphthalimide with alkenes.[12,13] If an electron-transfer mechanism does operate in the relatively non-polar solvents (benzene or acetone) used in our studies, it seems that subsequent proton transfer and cyclization is not greatly affected by chloro- or methoxycarbonyl-substituents in the phthalimide ring. However, the pyridinedicarboximides (**20**) and (**22**) yielded single photoproducts in moderate isolated yields (32 and 24%, respectively). For photoproduct (**23**) the appearance of a doublet (*J* 2 Hz) at δ_H 8.78 suggests that the isomer (**23b**) has been obtained. However, for photoproduct (**21**) the ^1H n.m.r. spectra do not enable us to make a definite assignment of the orientation of cyclization, because the ^1H n.m.r. signals for all the pyridine ring protons are shifted significantly in the product compared with the substrate.

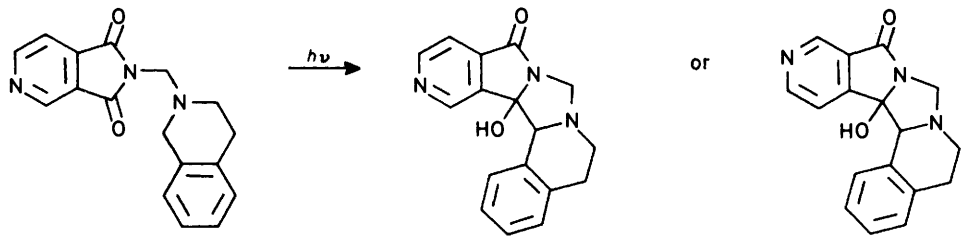
The naphthalene-2,3-dicarboximide derivatives (**24**)—(**26**) undergo a similar photocyclization to give (**27**)—(**29**) in good yield. The quantum yields for these reactions are similar (within a factor of 2) to those for the reactions of the corresponding phthalimides (**1**)—(**3**), as well as the substituted phthalimides (**7**)—(**9**) and (**12**), as judged qualitatively by the rates at which reaction occurs for equal concentrations of substrate absorbing almost all of the appropriate wavelengths from the irradiation source.

From the u.v. absorption spectra, the energy of the lowest excited singlet state of (**24**) is estimated to be 340 kJ mol^{-1}, and this state is (π,π^*) in nature. The (π,π^*) singlet state of (**1**), the corresponding phthalimide,[4] is at about 380 kJ mol^{-1}, and (**1**) has a lower lying (n,π^*) singlet state at 335 kJ mol^{-1}. From phosphorescence spectra, the energy of the lowest triplet state of (**24**) is 250 kJ mol^{-1}, compared with 290 kJ mol^{-1} for (**1**). For the naphthalenedicarboximide the lowest singlet and triplet states are undoubtedly (π,π^*) in nature, and the observed efficiency of the photochemical reaction for this and related compounds supports the proposal that the initial step in the cyclization reaction is electron transfer from the amine to the excited imide group. Such a process need not be greatly affected by the electronic nature or the energy of the lowest excited state of the imide (as has been demonstrated[14] for the photoreduction of aromatic ketones by amines), unlike direct hydrogen-atom abstraction which would be much slower and less efficient for a naphthalene derivative.

The photocyclization of (**3**), (**7**)—(**9**), (**12**), (**20**), (**22**), and (**26**) gives product mixtures from which one diastereoisomer of each of the corresponding pentacyclic or hexacyclic products can be isolated in moderate or good yield. T.l.c. and h.p.l.c. (high-performance liquid chromatography) analysis shows that there is no more than a small amount (< 5%) of any component that might be the other diastereoisomer, although in the case of imide (**3**) the second diastereoisomer can be isolated if the reaction is carried out in toluene (3%, *cf.* 72% of the major isomer) or in acetonitrile (12%, *cf.* 63% of the major isomer). The major diastereoisomer is almost certainly the one (**30**) with the bridgehead OH and H groups *trans*; molecular models suggest that there is severe steric interaction in the other isomer of these fused-ring systems, and the spectral data for the major and minor isomer of (**6**) are in keeping with the arguments developed below for the less rigid systems.



(20) (21a) (21b)



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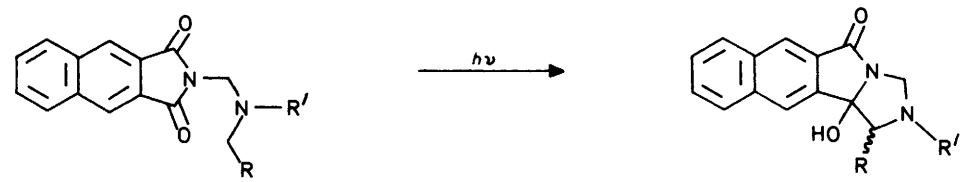
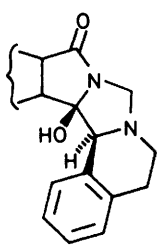


(24)	R = Ph, R' = CH_2Ph	(27)
(25)	R = $CH{=}CH_2$, R' = $CH_2CH{=}CH_2$	(28)
(26)	RR' = o-$C_6H_4CH_2CH_2$	(29)

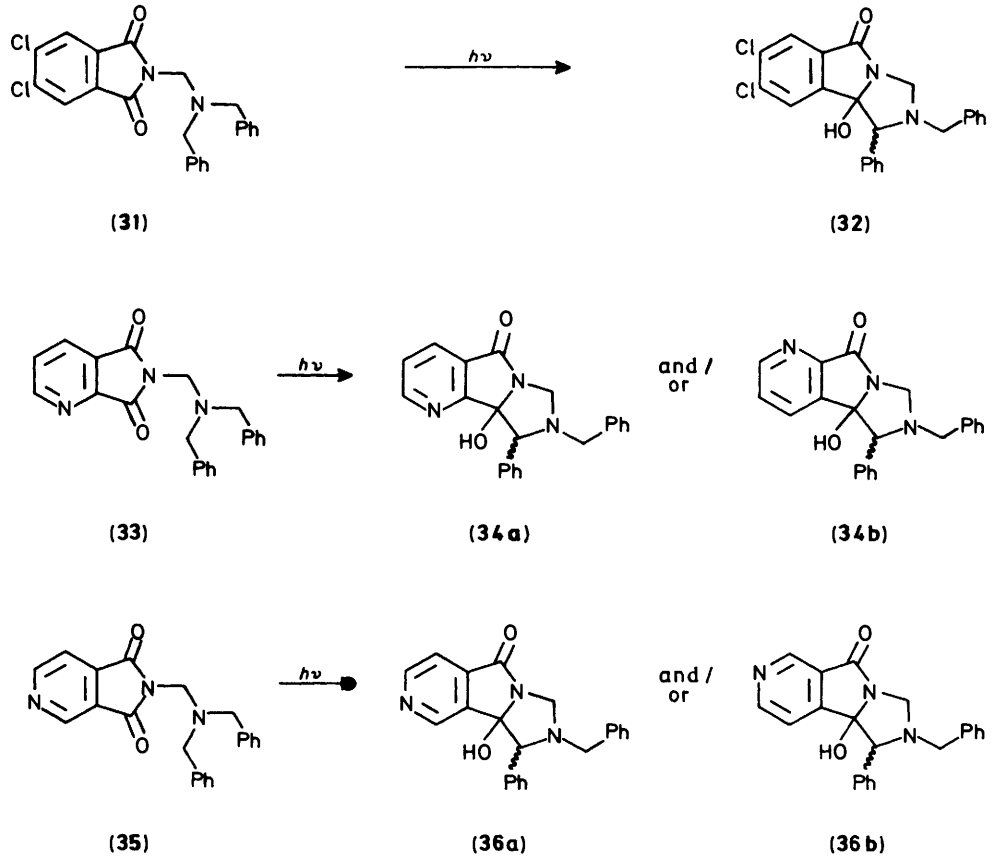


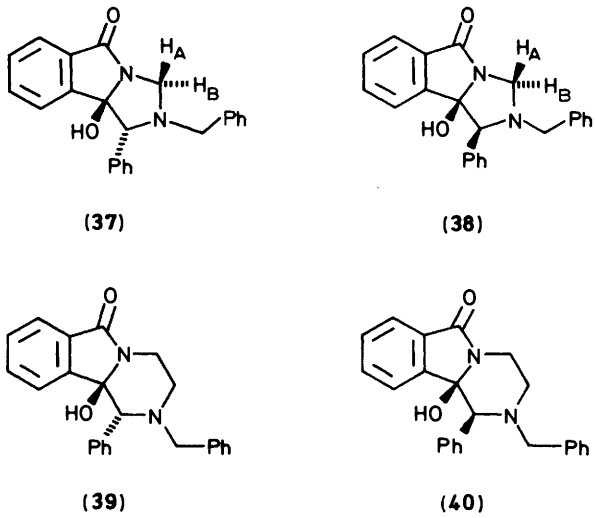
(30)

Imides (**1**), (**2**), (**24**), and (**25**), and also (**31**), (**33**), and (**35**), give mixtures of diastereoisomers that can be separated in some cases by crystallization or by column chromatography. In the case of imide (**35**), a small amount of a regioisomeric product [probably (**36a**)] was also obtained. The assignment of relative stereochemistry to the diastereoisomers can be made on the basis of n.m.r. data; the argument is presented here for the isomers (**37**) and (**38**) of product (**4**), and very similar results are obtained in the other cases.

In the ^{13}C n.m.r. spectrum of (**37**), the signals for the quaternary C(OH) carbon and the methine CH(Ph) carbon are at higher field (δ_C 94.0 and 73.8 p.p.m. respectively) than the corresponding signals (δ_C 98.5 and 78.0 p.p.m.) in the spectrum of (**38**). This arises from steric compression in the more hindered isomer (**37**), which is partially relieved by a slight lengthening of the (HO)C–C(Ph) bond. Similar differences in chemical-shift values have been observed in a number of cyclohexane derivatives,[15] where the more hindered stereoisomer gives signals at lower chemical-shift values. A theoretical justification for the effect has been proposed.[16] The carbonyl carbon atom in (**37**) also produces a signal at higher field (δ_C 171.1 p.p.m.) than that in (**38**) (δ_C 174.0 p.p.m.). This may also reflect the greater steric strain in (**37**), which is relieved to some extent by the cyclic amide group becoming more nearly planar. Such a change in the amide group is supported by the positions of the C=O stretching bands in the i.r. spectra, which are at 1 695 cm^{-1} for (**38**), but at 1 675 cm^{-1} for (**37**) which is closer to the value for an unconstrained aromatic five-membered lactam.

Diastereoisomeric fused hexahydropyrazines (**39**) and (**40**), obtained by irradiation of *N*-[2-(dibenzylamino)ethyl]-phthalimide, are homologues of (**37**) and (**38**) but should be less strained because of the larger size of the new ring. The i.r. spectra of (**39**) and (**40**) both show a C=O stretching band at 1 675—1 680 cm^{-1}, and the signals in the ^{13}C n.m.r. spectra for the quaternary carbon and the carbonyl carbon are no longer so different for the two isomers—δ_C 86.9 and 166.0 p.p.m. for (**39**),





87.0 and 164.5 p.p.m. for (**40**). The carbonyl signals for (**39**) and (**40**) are in the normal range for aromatic lactams.

However, there is still a marked difference in the positions of the ^{13}C n.m.r. signals for the methine carbon—δ_C 69.6 p.p.m. for (**39**) and 76.6 p.p.m. for (**40**)—and for the benzylic methylene carbon—δ_C 43.3 and 52.4 p.p.m. respectively. The effect on the benzylic carbon may arise because compound (**39**) can adopt a cage-like conformation in which this carbon lies above the benzene ring of the aromatic lactam part of the molecule. Similar effects have been noted[11,17] for the photoproducts derived from other unsaturated imides.

In the ^1H n.m.r. spectrum of (**37**), the protons of the NCH_2N group in the ring give rise to an AB pattern at δ_H 4.0 and 4.4 (J 6 Hz). H_A (signal at δ_H 4.4) is the proton *cis* to the OH group and closer to the lone pair of the bridgehead nitrogen, which is not completely planar; such an effect of a nitrogen lone pair is well documented for quinolizidine,[18] where there is a 0.8 p.p.m. difference in the signals for axial and equatorial hydrogens adjacent to the bridgehead nitrogen. In compound (**37**) H_B experiences a deshielding effect caused by the phenyl group on the carbon atom of the ring, because the preferred orientation of this group is 'edge on' with respect to the five-membered ring. In compound (**38**) the deshielding effect of the phenyl group is experienced more strongly by H_A than by H_B, with the result that the difference in chemical shifts is much larger—4.8 p.p.m. for H_A and 3.7 p.p.m. for H_B. Other factors may contribute to the difference in the AB pattern for the two stereoisomers, particularly the influence of the lone pair on the other (amine) nitrogen of the imidazolidine ring. If the bulky benzyl group on this nitrogen atom adopts, in each isomer, an *anti* relationship to the phenyl group on the adjacent carbon, this too would lead to a lower-field signal for H_A in isomer (**38**) because this proton would be in a *syn* relationship to the lone pair on the amine nitrogen. The signal for the methine proton in (**37**) is at δ_H 3.50 and for the methine proton in (**38**) is at δ_H 4.05. This difference probably reflects the influence of the adjacent hydroxy group, which is *cis* to the proton in (**37**) but *trans* in (**38**). A similar effect has been observed for the *cis* and *trans* protons of the $-CH_2-CH(OH)-$ unit in acenaphthenol.[19]

These n.m.r. data provide strong support for the assignment of relative stereochemistry in the photoproducts. Conclusive confirmation comes from a single-crystal *X*-ray crystallographic investigation of the structure of one diastereoisomer of compound (**4**). The molecular structure obtained from the

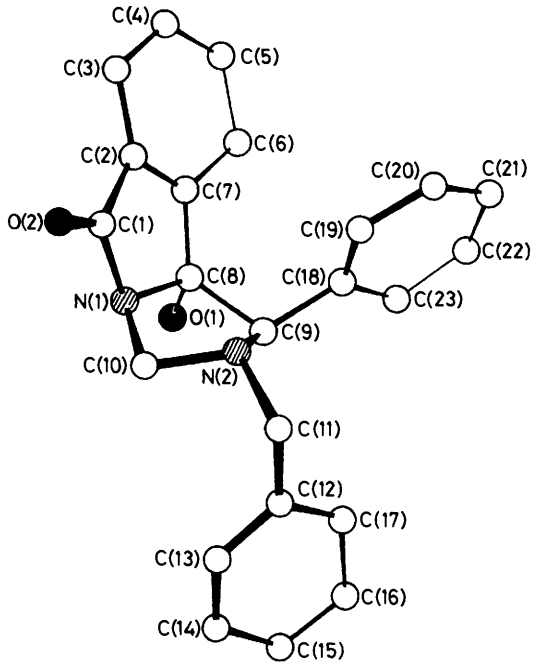
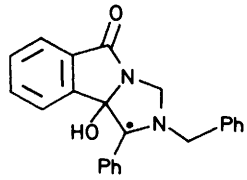


Figure. *X*-Ray molecular structure of compound (**37**), showing crystallographic numbering scheme

investigation is illustrated in the Figure, which also shows the crystallographic numbering system. The most significant feature for establishment of the relative configuration at the bridgehead positions is that the OH group [C(8)–O(1)] and the phenyl substituent [C(9)–C(18)] are clearly in a *trans* arrangement. The dihedral angle between these groups [as viewed along the C(8)–C(9) bond and projected onto a plane perpendicular to the bond] is 113°; for a planar five-membered ring a value of 120° is expected for *trans* substituents. This diastereoisomer is the one assigned structure (**37**) on the basis of the n.m.r. arguments.

When compound (**1**) is irradiated in benzene, the ratio of diastereoisomers of (**4**) remains constant at about 2.2:1 (as estimated by h.p.l.c. analysis) throughout the irradiation. However, in acetone this ratio changes from 1.9:1 in the early stages to 1:6.3 towards the end of the reaction; this provides a basis for preparing the second diastereoisomer in reasonable yield. In contrast, the ratio of diastereoisomers from the naphthalene-2,3-dicarboximide (**24**) remains constant in either benzene (1.5:1) or acetone (1.8:1). We attribute this difference to the fact that acetone competes effectively with (**1**) and (**4**), but not with (**24**) and (**27**), for absorbing useful light (mainly at 297, 303, and 313 nm) from the Pyrex-filtered output of a medium-pressure mercury arc; this is because the naphthalene derivatives absorb much more strongly in this region than do the benzene derivatives. The effect of absorption by acetone is to provide a route for sensitizing the interconversion of the isomers of (**4**). This could be by way of energy transfer and cleavage/recombination of the (HO)C–N(CO) bond, which would be consistent with the observed faster rate of reaction of (**1**) in acetone. Alternatively, the process could be an example of chemical sensitization *via* the stabilized radical (**41**). In either case the result is the formation of a higher proportion of the thermodynamically more stable stereoisomer.

The individual diastereoisomers of (**4**) and (**27**) were irradiated separately in benzene and in acetone. Only for (**4**) in acetone was there clear evidence (h.p.l.c.) for significant conversion of one stereoisomer into the other, although in all



(**41**)

cases there was eventually extensive photodegradation of the compounds.

Experimental

I.r. spectra were recorded on a Perkin-Elmer 297 instrument, n.m.r. spectra on a Jeol E60 HL or a Bruker Aspect 200 instrument, and mass spectra on a Hitachi Perkin-Elmer RMS-4 instrument. For column chromatography the silica used was Merck Kieselgel 60, Art 7734, or Kieselgel 60 H, Art 7736. M.p.s are uncorrected.

Preparation of Mannich Bases.—An equimolar mixture of the imide,* formaldehyde (40% aqueous solution), and the secondary amine was warmed in ethanol until the mixture became homogeneous. The solution was cooled, and the Mannich base was filtered off, and in some cases further purified by recrystallization. Data for compounds (**1**),[5] (**2**),[3] and (**3**)[20] have been reported previously. The following compounds were thus prepared.

4,5-*Dichloro*-N-[(1,2,3,4-*tetrahydroisoquinolin*-2-*yl*)*methyl*]-*phthalimide* (**7**) was obtained in 76% yield (54% after recrystallization from benzene), m.p. 164—166 °C; $\nu_{max.}$(Nujol) 1 780 and 1 710 cm^{-1}; δ_H($CDCl_3$) 8.10 (2 H, s), 7.20 (4 H, s), 4.87 (2 H, s), 3.85 (2 H, s), and 2.95 (4 H, s); *m*/*z* 360 (M^+), 230, 228, 146, 145, 132 (base), and 104 (Found: C, 59.9; H, 3.9; N, 7.9; Cl, 19.7. $C_{18}H_{14}Cl_2N_2O_2$ requires C, 59.83; H, 3.87; N, 7.76; Cl, 19.67%).

3-*Chloro*-N-[(1,2,3,4-*tetrahydroisoquinolin*-2-*yl*)*methyl*]-*phthalimide* (**8**) was obtained in 85% yield (64% after recrystallization from ethanol), m.p. 131—133 °C; $\nu_{max.}$(Nujol) 1 770 and 1 710 cm^{-1}; δ_H($CDCl_3$) 7.9—7.6 (3 H, m), 7.06 (4 H, s), 4.83 (2 H, s), 3.86 (2 H, s), and 3.15—2.75 (4 H, m); *m*/*z* 328 and 326 (M^+), 194, 145 (base), and 132 (base) (Found: C, 65.9; H, 4.65; N, 8.6; Cl, 11.0. $C_{18}H_{15}ClN_2O_2$ requires C, 66.16; H, 4.59; N, 8.58; Cl, 10.87%).

4-*Chloro*-N-[(1,2,3,4-*tetrahydroisoquinolin*-2-*yl*)*methyl*]-*phthalimide* (**9**) was obtained in 89% yield, m.p. 115—118 °C; $\nu_{max.}$(Nujol) 1 780 and 1 710 cm^{-1}; δ_H($CDCl_3$) 7.9—7.5 (3 H, m), 7.0 (4 H, s), 4.75 (2 H, s), 3.80 (2 H, s), and 2.90 (4 H, s); *m*/*z* 326 (M^+), 196, 194, 146, 145, 132 (base), and 104 (Found; C, 66.0; H, 4.65; N, 8.6; Cl, 10.9%).

3-*Nitro*-N-[(1,2,3,4-*tetrahydroisoquinolin*-2-*yl*)*methyl*]-*phthalimide* (**10**) was obtained in 71% yield (54% after recrystallization from ethanol), m.p. 171—173 °C; $\nu_{max.}$(Nujol) 1 780 and 1 710 cm^{-1}; δ_H($CDCl_3$) 8.4—7.9 (3 H, m), 7.20 (4 H, s), 4.90 (2 H, s), 3.90 (2 H, s), and 3.00 (4 H, s); *m*/*z* 337 (M^+), 320, 290, 205, 192, 145 (base), 132, 117, and 104 (Found: C, 64.0; H, 4.5; N, 12.5. $C_{18}H_{15}N_3O_4$ requires C, 64.09; H, 4.45; N, 12.46%).

4-*Nitro*-N-[(1,2,3,4-*tetrahydroisoquinolin*-2-*yl*)*methyl*]-*phthalimide* (**11**) was obtained in 58% yield (33% after recrystallization from ethanol), m.p. 146—148 °C; $\nu_{max.}$(Nujol) 1 775 and 1 710 cm^{-1}; δ_H($CDCl_3$) 8.66 (1 H, br, s), 8.62 (1 H, dd, *J* 8 and 2 Hz), 8.07 (1 H, d, *J* 8 Hz), 7.1 (4 H, s), 4.88 (2 H, s), 3.85

* Many of the imides were made according to the methods described in G. B. Bachman and R. S. Barker, *J. Org. Chem.*, 1949, **14**, 102, or G. C. Crockett, B. J. Swanson, D. R. Anderson, and T. H. Koch, *Synth. Commun.*, 1981, **11**, 447.

(2 H, s), and 3.1—2.8 (4 H, m); *m/z* 337 (M^+), 205, 192, 145 (base), and 132 (base) (Found: C, 63.9; H, 4.55; N, 12.6%).

4-*Methoxycarbonyl*-N-[(1,2,3,4-*tetrahydroisoquinolin*-2-*yl*)-*methyl*]*phthalimide* (**12**) was obtained in 39% yield after repeated column chromatography (silica gel; chloroform–methanol) and recrystallization from ethanol, m.p. 100—103 °C; $\nu_{max.}$(Nujol) 1 770 and 1 710 cm^{-1}; $\delta_H(CDCl_3)$ 8.42 (1 H, m), 8.36 (1 H, dd, *J* 6.5 and 1 Hz), 7.96 (1 H, d, *J* 6.5 Hz), 7.07 (4 H, s), 4.90 (2 H, s), 4.02 (3 H, s), 3.91 (2 H, s), and 3.0 (4 H, m); $\delta_C[(CD_3)_2SO]$ 167.8, 164.7, 135.0, 134.9, 134.3, 133.5, 132.0, 128.3, 126.2, 125.7, 125.3, 123.5, 122.9, 59.2, 52.7, 52.0, 47.9, and 28.6 p.p.m.; *m/z* 349, 205, 146, 145, 144, 132 (base), and 104 (Found: C, 68.5; H, 5.2; N, 8.0. $C_{20}H_{18}N_2O_4$ requires C, 68.57; H, 5.15; N, 8.00%).

N-[(1,2,3,4-*Tetrahydroisoquinolin*-2-*yl*)*methyl*]*pyridine*-2,3-*dicarboximide* (**20**) was obtained in 68% yield (46% after recrystallization from ethanol), m.p. 153—156 °C; $\nu_{max.}$(Nujol) 1 780 and 1 720 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.99 (1 H, dd, *J* 5 and 2 Hz), 8.32 (1 H, dd, *J* 8 and 2 Hz), 7.88 (1 H, dd, *J* 8 and 5 Hz), 7.06 (4 H, s), 4.68 (2 H, s), 3.75 (2 H, s), and 2.85 (4 H, m); $\delta_C(CDCl_3)$ 167.2, 155.5, 134.3, 133.6, 131.3, 128.7, 127.5, 126.5, 126.1, 125.6, 59.7, 52.7, 48.8, and 29.3 p.p.m.; *m/z* 145 (base), 132, 117, and 105 (Found: C, 69.5; H, 5.2; N, 14.2. $C_{17}H_{15}N_3O_2$ requires C, 69.62; H, 5.15; N, 14.33%).

N-[(1,2,3,4-*Tetrahydroisoquinolin*-2-*yl*)*methyl*]*pyridine*-3,4-*dicarboximide* (**22**) was obtained in 58% yield (29% after recrystallization from ethanol), m.p. 121—124 °C; $\nu_{max.}$(Nujol) 1 780 and 1 715 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 9.14 (1 H, d, *J* 2 Hz), 9.11 (1 H, d, *J* 5 Hz), 7.90 (1 H, dd, *J* 5 and 2 Hz), 7.06 (4 H, s), 4.66 (2 H, s), 3.74 (2 H, s), and 2.85 (4 H, m); $\delta_C(CDCl_3)$ 167.9, 155.8, 145.2, 133.7, 128.8, 126.7, 126.3, 125.8, 117.0, 60.0, 52.8, 48.9, and 29.4 p.p.m.; *m/z* 160, 145 (base), 132 (base), 117, and 104 (Found: C, 69.6; H, 5.2; N, 14.25%).

Naphthalene-2,3-dicarboximide was prepared from the corresponding diacid *via* the anhydride in 84% yield, m.p. 275—277 °C (lit.,[21] 275 °C); $\nu_{max.}$(Nujol) 3 300, 1 770, and 1 710 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.24 (2 H, s), 8.2—7.9 and 7.9—7.8 (4 H, m), and 6.4 (1 H, br); *m/z* 197 (M^+, base), 172, 154, and 126 (Found: C, 73.3; H, 3.6; N, 7.2. Calc. for $C_{12}H_7NO_2$: C, 73.10; H, 3.56; N, 7.10%).

N-(*Dibenzylaminomethyl*)*naphthalene*-2,3-*dicarboximide* (**24**) was obtained in 70% yield after recrystallization from ethanol, m.p. 163—164 °C; $\nu_{max.}$(Nujol) 1 770 and 1 700 cm^{-1}; $\delta_H(CDCl_3)$ 8.30 (2 H, s), 7.9—7.4 (4 H, m), 7.3—7.0 (10 H, m), 4.78 (2 H, s), and 3.83 (4 H, s); *m/z* 406 (M^+), 315, 210, 196, 118, and 91 (base) (Found: C, 79.95; H, 5.45; N, 6.8. $C_{27}H_{22}N_2O_2$ requires C, 79.77; H, 5.46; N, 6.89%).

N-(*Diallylaminomethyl*)*naphthalene*-2,3-*dicarboximide* (**25**) was obtained in 34% yield after recrystallization from ethanol, m.p. >225 °C (decomp.); $\nu_{max.}$(Nujol) 1 760 and 1 700 cm^{-1}; $\delta_H(CDCl_3)$ 8.40 (2 H, s), 8.25—7.75 (4 H, m), 6.3—5.05 (6 H, m), 4.75 (2 H, s), and 3.37 (4 H, d, *J* 6 Hz); *m/z* 306 (M^+), 210, 126, 110, and 96 (base) (Found: C, 74.3; H, 6.0; N, 9.0. $C_{19}H_{18}N_2O_2$ requires C, 74.51; H, 5.88; N, 9.15%).

N-[(1,2,3,4-*Tetrahydroisoquinolin*-2-*yl*)*methyl*]*naphthalene*-2,3-*dicarboximide* (**26**) was obtained in 52% yield after column chromatography (silica gel; chloroform) and recrystallization from ethanol, m.p. 181.5—183 °C; $\nu_{max.}$(Nujol) 1 760 and 1 700 cm^{-1}; $\delta_H(CDCl_3)$ 8.47 (2 H, s), 8.25—7.5 (4 H, m), 7.10 (4 H, s), 4.90 (2 H, s), 3.90 (2 H, s), and 3.1—2.9 (4 H, m); *m/z* 342 (M^+), 210, 196, 146, and 132 (base) (Found: C, 77.0; H, 5.4; N, 8.1. $C_{22}H_{18}N_2O_2$ requires C, 77.14; H, 5.30; N, 8.19%).

4,5-*Dichloro*-N-(*dibenzylaminomethyl*)*phthalimide* (**31**) was obtained in 51% yield, m.p. 145—148 °C; $\nu_{max.}$(Nujol) 1 770 and 1 710 cm^{-1}; $\delta_H(CDCl_3)$ 7.78 (2 H, s), 7.26 (10 H, m), 4.11 (2 H, s), and 3.69 (4 H, s); *m/z* 428, 426, and 424 (M^+), 210, 196, 118, and 91 (base) (Found: C, 65.1; H, 4.4; N, 6.8; Cl, 16.95. $C_{23}H_{18}Cl_2N_2O_2$ requires C, 64.95; H, 4.27; N, 6.59; Cl, 16.68%).

N-(*Dibenzylaminomethyl*)*pyridine*-2,3-*dicarboximide* (**33**) was obtained in 43% yield, m.p. 132—135 °C; $\nu_{max.}$(Nujol) 1 770 and 1 710 cm^{-1}; $\delta_H(CDCl_3)$ 8.80 (1 H, dd, *J* 5 and 2 Hz), 8.00 (1 H, dd, *J* 8 and 2 Hz), 7.45 (1 H, dd, *J* 8 and 5 Hz), 7.35—6.95 (10 H, m), 4.70 (2 H, s), and 3.70 (4 H, s); $\delta_C(CDCl_3)$ 167.2, 155.3, 139.0, 131.1, 128.7, 128.2, 127.2, 57.4, and 56.4 p.p.m.; *m/z* 357 (M^+), 266, 206, 196, 161, 118, 91 (base), and 77 (Found: C, 73.75; H, 5.5; N, 11.9. $C_{23}H_{19}N_3O_2$ requires C, 73.95; H, 5.32; N, 11.76%).

N-(*Dibenzylaminomethyl*)*pyridine*-3,4-*dicarboximide* (**35**) was obtained in 42% yield, m.p. 176—179 °C; $\nu_{max.}$(Nujol) 1 770 and 1 710 cm^{-1}; $\delta_H(CDCl_3)$ 9.15 (1 H, d, *J* 1 Hz), 9.05 (1 H, d, *J* 5 Hz), 7.70 (1 H, dd, *J* 5 and 1 Hz), 7.5—7.05 (10 H, m), 4.75 (2 H, s), and 3.75 (4 H, s); *m/z* 357 (M^+), 266 (base), 196, 161, 118, and 91 (Found: C, 73.9; H, 5.4; N, 11.8%).

Irradiations.—These were carried out under nitrogen in a reactor vessel of 350 cm^3 capacity. The solvent was benzene or acetone, and the light source was a Hanovia 450-W medium-pressure mercury arc with a Pyrex water-cooling jacket.

Data have been reported previously for one diastereoisomer of photoproducts (**4**),[22] (**5**),[3] and (**6**);[20] yields have been improved to 60% for (**4**), 40% for (**5**), and 90% for (**6**).

4-*Benzyl*-2-*hydroxy*-3-*phenyl*-4,6-*diazatricyclo*[6.4.0.0^{2,6}]-*dodeca*-1(12),8,10-*trien*-7-*one* (**4**). The second diastereoisomer was isolated by silica gel chromatography ($CHCl_3$ eluant) of the product mixture obtained by irradiation of (**1**) (0.020 mol) in acetone for 12 h. The crude product was recrystallized from cyclohexane (yield 43%), m.p. 152—155 °C; $\nu_{max.}$(Nujol) 3 270 and 1 695 cm^{-1}; $\delta_H(CDCl_3)$ 8.0—6.7 (13 H, m), 6.7—6.35 (1 H, m), 4.75 (1 H, d, *J* 7 Hz), 4.06 (1 H, s), 3.66 (1 H, d, *J* 7 Hz), 3.37 (1 H, d, *J* 13 Hz), and 3.75 (1 H, d, *J* 13 Hz); $\delta_C(CDCl_3)$ 174.0, 146.9, 137.5, 132.6, 131.3, 128.1, 127.1, 126.4, 124.1, 123.2, 98.5, 78.0, 64.7, and 55.3 p.p.m. (Found: C, 77.6; H, 5.9; N, 8.0. $C_{23}H_{20}N_2O_2$ requires C, 77.51; H, 5.66; N, 7.86%).

4-*Allyl*-2-*hydroxy*-3-*vinyl*-4,6-*diazabicyclo*[6.4.0.0^{2,6}]-*dodeca*-1(12),8,10-*trien*-7-*one* (**5**). Pure samples of the two diasteroisomers were isolated by h.p.l.c. separation (spherisorb 5μm silica; chloroform–hexane) of the product mixture (63%). First isomer, m.p. 124—126 °C; $\delta_H(CDCl_3)$ 7.65—7.25 (4 H, m), 6.1—4.7 (6 H, m), 4.62 (1 H, d, *J* 7 Hz), 4.15 (1 H, br), 3.65 (1 H, d, *J* 7 Hz), 3.45 (1 H, d, *J* 7 Hz), 3.3 (1 H, m), and 2.95 (1 H, m); $\delta_C(CDCl_3)$ 172.5, 145.7, 134.5, 133.0, 131.9, 129.7, 124.5, 123.8, 119.7, 117.6, 97.2, 73.9, 63.9, and 54.1 p.p.m. Second isomer, m.p. 109—110 °C; $\delta_H(CDCl_3)$ 7.8—7.4 (4 H, m), 6.2—5.0 (6 H, m), 4.47 (1 H, d, *J* 6 Hz), 4.00 (1 H, d, *J* 6 Hz), 3.7 (1 H, s, reduced with D_2O), 3.45 (1 H, m), 2.80 (1 H, dd, *J* 13 and 8 Hz), and 2.70 (1 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 170.9, 145.0, 133.4, 133.0, 132.6, 132.0, 130.3, 124.2, 123.0, 122.2, 118.7, 94.6, 72.8, 64.8, and 54.6 p.p.m.

2-*Hydroxy*-10,12-*diazapentacyclo*[10.8.0.0.^{2,10}0.^{3,8}0^{15,20}]-*icosa*-3(8),4,6,15(20),16,18-*hexaen*-9-*one* (**6**). The second diastereoisomer (12%) was isolated by silica-gel chromatography (chloroform–methanol eluant) of the product mixture obtained by irradiation of (**3**) (0.017 mol) in acetonitrile for 13 h; $\delta_H(CDCl_3)$ 7.6—6.9 (8 H, m), 4.52 (1 H, d, *J* 9 Hz), 3.95 (1 H, d, *J* 9 Hz), 3.6 (1 H, br), 3.42 (1 H, s), and 2.9—2.6 (4 H, m); $\delta_C(CDCl_3)$ 171.1, 146.3, 135.9, 133.1, 132.0, 130.3, 129.9, 128.8, 127.5, 127.1, 125.7, 123.9, 123.7, 95.9, 66.1, 65.5, 48.4, and 28.8 p.p.m.

5,6-*Dichloro*-2-*hydroxy*-10,12-*diazapentacyclo*[10.8.0.0.^{2,10}-0.^{3,8}0^{15,20}]*icosa*-3(8),4,6,15(20),16,18-*hexaen*-9-*one* (**13**). After irradiation of (**7**) (0.0138 mol) in benzene for 9 h the solution was filtered, concentrated to half volume, and filtered again, to give the *title compound* (**13**) in 34% yield, m.p. 167—169 °C; $\nu_{max.}$(Nujol) 3 325 and 1 695 cm^{-1}; $\delta_H(CDCl_3)$ 7.5—6.7 (6 H, m), 4.65 (1 H, d, *J* 11 Hz), 4.40 (1 H, s), 4.30 (1 H, d, *J* 11 Hz), and 2.9—1.7 (4 H, m); $\delta_C(CDCl_3)$ 171.5, 148.8, 135.7, 133.7, 133.1,

131.9, 130.8, 129.0, 127.9, 127.6, 126.8, 126.3, 125.9, 97.2, 68.6, 67.8, 45.2, and 28.2 p.p.m.; *m/z* 215, 145, 132 (base), and 117 (Found: C, 59.6; H, 3.9; N, 7.9; Cl, 19.9. $C_{18}H_{14}Cl_2N_2O_2$ requires C, 59.83; H, 3.87; N, 7.76; Cl, 19.67%).

4-*Chloro-* (**14**) and 7-*chloro*-2-*hydroxy*-10,12-*diazapentacyclo*[10.8.0.0.^{2,10}0.^{3,8}0^{15,20}]*icosa*-3(8),4,6,15(20),16,18-*hexaen*-9-*one* (**15**). After irradiation of (**8**) (0.012 mol) in benzene for 15 h, the solvent was evaporated and the residue separated by silica-gel chromatography with chloroform–light petroleum (b.p. 60—80 °C) as eluant. The crude products were recrystallized from ethanol. The major isomer (**15**) had m.p. 167—170 °C; $\nu_{max.}$(Nujol) 3 350 and 1 680; δ_H($CDCl_3$) 7.7—7.55 (1 H, m), 7.35—6.9 (6 H, m), 4.85 (1 H, d, *J* 11 Hz), 4.71 (1 H, s), 4.47 (1 H, d, *J* 11 Hz), 3.2 (1 H, br), and 2.95—2.15 (4 H, m); δ_C($CDCl_3$) 171.3, 150.7, 133.7, 131.2, 128.7, 128.0, 127.4, 125.9, 123.0, 96.5, 68.8, 67.9, 45.6, and 28.5; *m/z* 145 (base), 132, and 117 (Found: C, 66.1; H, 4.6; N, 8.5; Cl, 11.1. $C_8H_{15}ClN_2O_2$ requires C, 66.16; H, 4.59; N, 8.58; Cl, 10.87%). Compound (**14**) had m.p. 167—169 °C; $\nu_{max.}$(Nujol) 3 350 and 1 680 cm^{-1}; δ_H($CDCl_3$) 7.8—7.1 (7 H, m); 5.00 (1 H, d, *J* 8 Hz), 4.24 (1 H, d, *J* 8 Hz), 4.16 (1 H, s), 3.75—3.45 (2 H, m), 3.25 (1 H, br), and 3.1—2.5 (2 H, m) (Found: C, 65.4; H, 5.15; N, 8.25; Cl, 10.65%).

5-*Chloro*-(**16**) and 6-*chloro*-2-*hydroxy*-10,12-*diazapentacyclo*-[10.8.0.0.^{2,10}0.^{3,8}0^{15,20}]*icosa*-3(8),4,6,15(20),16,18-*hexaen*-9-*one* (**17**). After irradiation of (**9**) (0.021 mol) in benzene for 27 h, a sample (14%) of the product (**16**) was removed by filtration. The solvent was evaporated and the residue was separated by silica-gel chromatography with chloroform–light petroleum (b.p. 60—80 °C) as eluant to give a mixture of compounds (**16**) and (**17**) in 46% yield. *Compound* (**16**) had m.p. 174—177 °C; $\nu_{max.}$(Nujol) 3 350 and 1 685 cm^{-1}; δ_H($CDCl_3$) 7.9—7.0 (8 H, m), 4.85 (1 H, d, *J* 12 Hz), 4.73 (1 H, s), 4.48 (1 H, d, *J* 12 Hz), and 2.9—1.8 (5 H, m); δ_C[$(CD_3)_2SO$] 172.0, 150.0, 139.4, 135.0, 134.0, 131.9, 131.2, 129.9, 129.2, 128.8, 127.3, 126.6, 125.2, 98.5, 70.1, 68.4, 49.6, and 29.2 p.p.m.; *m/z* 145 and 132 (base) (Found: C, 65.95; H, 4.6; N, 8.6; Cl, 10.9. $C_{18}H_{15}ClN_2O_2$ requires C, 66.16; H, 4.59; N, 8.58; Cl, 10.87%). The crude product mixture (75%) obtained after chromatographic separation of a second irradiation mixture was subjected to high-field (400 MHz) ^{1}H n.m.r. analysis; δ_H($CDCl_3$) 7.54 (br d, *J* 7.5 Hz), 7.40 (dd, *J* 2 and 0.5 Hz), 7.39 (dd, *J* 8 and 0.5 Hz), 7.28 (br m), 7.19 (dd, *J* 8 and 2 Hz), 7.16 (m), 7.115 (dd, *J* 8 and 2 Hz), 6.98 (dd, *J* 2 and 0.5 Hz), 6.945 (br m), 6.91 (dd, *J* 8 and 0.5 Hz), 5.2 (br), 4.612 (d, *J* 11 Hz), 4.610 (d, *J* 11 Hz), 4.48 (s), 4.34 (d, *J* 11 Hz), 4.33 (d, *J* 11 Hz), 2.8—2.7 (m), 2.62—2.56 (m), 2.40 (br), 2.36 (br), 2.05 (t, *J* 3 Hz), 2.02 (m), and 1.99 (t, *J* 3 Hz). Repeated recrystallization of the mixture from benzene gave a small sample of pure (**16**), whose high-field ^{1}H n.m.r. spectrum showed signals corresponding to those at δ_H 6.98, 7.19, and 7.39 in the spectrum of the mixture, although the chemical-shift values were different by about 0.1 p.p.m.

2-*Hydroxy*-5-(*and* 6)-*methoxycarbonyl*-10,12-*diazapentacyclo*[10.8.0.0.^{2,10}0.^{3,8}0^{15,20}]*icosa*-3(8),4,6,15(20),16,18-*hexaen*-9-*one* (**18**) *and* (**19**). After irradiation of (**12**) (0.005 mol) in benzene for 4 h, the residue was purified by silica-gel chromatography with light petroleum (b.p. 60—80 °C)–ethyl acetate as eluant, to give a mixture (82%) of products (**18**) and (**19**). Further separation by column chromatography (silica-gel; chloroform) and h.p.l.c. (silica gel, 5μm spherisorb; chloroform–hexane) did not yield pure samples of the individual isomers. For the major isomer, δ_H($CDCl_3$) 8.02 (1 H, d, *J* 1.5 Hz), 7.85 (1 H, dd, *J* 5 and 1.5 Hz), 7.58 (1 H, d, *J* 6 Hz), 7.3—6.85 (4 H, m), 4.76 (1 H, d, *J* 9 Hz), 4.54 (1 H, s), 4.31 (1 H, d, *J* 9 Hz), 3.87 (3 H, s), and 3.0—1.9 (4 H, m); δ_C($CDCl_3$) 172.7, 165.6, 152.4, 134.8, 133.8, 133.0, 131.3, 129.9, 128.5, 127.8, 127.2, 125.7, 125.4, 124.3, 97.3, 68.4, 67.3, 52.2, 45.2, and 28.0 p.p.m.

2-*Hydroxy*-4-(*or* 7),10,12-*triazapentacyclo*[10.8.0.0.^{2,10}0.^{3,8}-0^{15,20}]*icosa*-3(8),4,6,15(20),16,18-*hexaen*-9-*one* (**21**). After irradiation of (**20**) (0.017 mol) in benzene for 9 h, the crude product was recrystallized from ethanol to give the product (**21**) in 36% yield, m.p. 155—158 °C; $\nu_{max.}$(Nujol) 3 200 and 1 710 cm^{-1}; δ_H[$(CD_3)_2SO$] 8.50 (1 H, dd, *J* 5 and 2 Hz), 7.93 (1 H, dd, *J* 8 and 2 Hz), 7.8—7.65 (1 H, m), 7.33 (1 H, dd, *J* 8 and 5 Hz), 7.2—6.8 (3 H, m), 4.79 (1 H, d, *J* 10 Hz), 4.58 (1 H, s), 4.35 (1 H, d, *J* 10 Hz), and 2.9—2.0 (4 H, m); δ_C($CDCl_3$) 170.5, 153.2, 133.3, 132.6, 129.6, 128.0, 127.0, 125.7, 124.4, 97.3, 69.1, 66.9, 46.0, and 28.2 p.p.m.; *m/z* 145 (base), 132 and 117 (Found: C, 69.7; H, 5.5; N, 13.95. $C_{17}H_{15}N_3O_2$ requires C, 69.62; H, 5.15; N, 14.33%).

2-*Hydroxy*-5(*or* 6),10,12-*triazapentacyclo*[10.8.0.0.^{2,10}-0.^{3,8}0^{15,20}]*icosa*-3(8),4,6,15(20),16.18-*hexaen*-9-*one* (**23**). After irradiation of (**22**) (0.017 mol) in benzene for 11 h, the crude precipitated product was recrystallized from ethanol to give the product (**23**) in 24% yield, m.p. 188—189 °C; $\nu_{max.}$(Nujol) 1 720 cm^{-1}; δ_H[$(CD_3)_2SO$] 8.78 (1 H, d, *J* 2 Hz), 8.51 (1 H, d, *J* 6 Hz), 7.65 (1 H, dd, *J* 6 and 2 Hz), 7.45—6.9 (4 H, m), 4.76 (1 H, d, *J* 11 Hz), 4.60 (1 H, s), 4.38 (1 H, d, *J* 11 Hz), and 2.9—1.8 (4 H, m); δ_C($CDCl_3$) 172.1, 153.0, 146.5, 133.6, 129.9, 129.0, 127.7, 126.1, 119.3, 97.7. 68.8, 68.2, 45.6, and 28.5 p.p.m.; *m/z* 145 (base) 132, 117, and 105 (Found: C, 69.6; H, 5.2; N, 14.4%).

13-*Benzyl*-11-*hydroxy*-12-*phenyl*-13,15-*diazatetracyclo*-[8.6.0.0.^{3,8}0^{11,15}]*hexadeca*-1(10),2,4,6,8-*pentaen*-16-*one* (**27**). After irradiation of (**24**) (0.0049 mol) in benzene for 45 min, the solvent was evaporated and the residue was separated by silica-gel column chromatography with 50:50 chloroform–light petroleum (b.p. 60—80 °C) as eluant. Crude product (**27**) (90%) was recrystallized from ethanol to give a pure diastereoisomer (40%), m.p. 210—212 °C; $\nu_{max.}$(Nujol) 3 300 and 1 690 cm^{-1}; δ_H($CDCl_3$) 8.2 (1 H, s), 7.9—7.1 (15 H, m), 4.52 (1 H, d, *J* 7 Hz), 4.16 (1 H, d, *J* 7 Hz), 3.99 (1 H, d, *J* 13 Hz), 3.8 (1 H, br), 3.52 (1 H, s), and 3.28 (1 H, d, *J* 13 Hz); δ_C($CDCl_3$) 170.5, 140.0, 137.0, 135.6, 134.5, 134.1, 129.8, 128.9, 127.7, 127.2, 125.2, 123.0, 94.0, 74.0, 65.1, and 56.6 p.p.m.; *m/z* 315, 210 (base), 196, and 91 (Found: C, 79.4; H, 5.55; N, 6.9. $C_{27}H_{22}N_2O_2$ requires C, 79.77; H, 5.46; N, 6.89%). The second stereoisomer was obtained (25%) as a second crop of crystals from ethanol, m.p. 186—188 °C; $\nu_{max.}$(Nujol) 3 220 and 1 695 cm^{-1}; δ_H($CDCl_3$) 7.8 (1 H, s), 7.75—7.25 (5 H, m), 7.18 (5 H, s), 7.02 (5 H, s), 4.80 (1 H, d, *J* 7 Hz), 4.15 (1 H, s), 3.80 (1 H, d, *J* 12 Hz), 3.71 (1 H, d, *J* 7 Hz), 3.7 (1 H, vbr), and 3.55 (1 H, d, *J* 12 Hz); δ_C($CDCl_3$) 172.7, 141.0, 137.6, 135.5, 133.3, 129.6, 128.2, 127.2, 126.9, 124.3, 123.7, 98.5, 77.0, 64.5, and 55.6 p.p.m.; *m/z* 315, 210, 196, and 91 (base) (Found: C, 79.6; H, 5.6; N, 6.9%).

13-*Allyl*-11-*hydroxy*-12-*vinyl*-13,15-*diazatetracyclo*-[8.6.0.0.^{3,8}0^{11,15}]*hexadeca*-1(10),2,4,6,8-*pentaen*-16-*one* (**28**). After irradiation of (**25**) (0.0168 mol) in benzene for 10 h, the crude product was purified by silica-gel chromatography with chloroform as eluant, followed by recrystallization from ethanol to give one diastereoisomer of compound (**28**) in 36% yield, m.p. 212—213 °C; $\nu_{max.}$(Nujol) 3 250 and 1 695 cm^{-1}; δ_H($CDCl_3$) 8.36 (1 H, s), 8.2—7.9 (3 H, m), 7.8—7.6 (2 H, m), 6.4—5.1 (6 H, m), 4.68 (1 H, d, *J* 7 Hz), 4.18 (1 H, d, *J* 7 Hz), 3.5 (1 H br), 3.38 (1 H, s), and 3.2—2.8 (2 H, m); δ_C[$(CD_3)_2SO$] 171.1, 135.7, 135.4, 129.0, 128.5, 128.2, 127.0, 123.9, 123.4, 118.3, 117.2, 99.8, 74.1, 63.5, and 54.2 p.p.m.; *m/z* 306, 265, 210, 183, 155, 127, 109, and 96 (base) (Found: C, 74.3; H, 6.0; N, 9.1. $C_{19}H_{18}N_2O_2$ requires C, 74.55; H, 5.88; N, 9.15%). A small sample of the other diastereoisomer was obtained in a reasonable degree of purity, m.p. 201—203 °C; δ_H($CDCl_3$) 8.27 (1 H, s), 8.15—7.75 (3 H, m), 7.75—7.5 (2 H, m), 6.3—5.0 (6 H, m), 4.91 (1 H, d, *J* 7.5 Hz), 4.4 (1 H, br), 4.11 (1 H, d, *J* 7.5 Hz), 3.95—3.75 (1 H, m), and 3.5—3.1 (2 H, m).

1-*Hydroxy*-11,13-*diazahexacyclo*[11.11.0.0.^{2,11}0.^{3,8}0.^{15,24}-0^{17,22}]*tetracosa*-3(8),4,6,15(24),16,18,20,22-*octaen*-14-*one* (**29**). After irradiation of (**26**) (0.0074 mol) in benzene for 2 h, the precipitated product was recrystallized from benzene to give the *product* (**29**) in 80% yield; m.p. 180—183 °C; $\nu_{max.}$(Nujol) 3 350

and 1 720 cm^{-1}; $\delta_H(CDCl_3)$ 8.17(1 H, s), 8.0—6.8 (9 H, m), 4.88 (1 H, d, *J* 12 Hz), 4.75 (1 H, s), 4.51 (1 H, d, *J* 12 Hz), and 3.0—2.0 (4 H, m); $\delta_C(CDCl_3)$ 171.5 (s), 142.2 (s), 135.6 (s), 133.4, 130.8, 129.6, 128.8, 128.2, 127.2, 127.0, 125.8, 125.5, 124.2, 97.6 (s), 69.1 (d), 68.1 (t), 45.5 (t), and 28.5 p.p.m. (t); *m/z* 197, 145 (base), 132, and 126 (Found: C, 77.0; H, 5.4; N, 8.1. $C_{22}H_{18}N_2O_2$ requires C, 77.14; H, 5.30; N, 8.19%).

4-Benzyl-10,11-dichloro-2-hydroxy-3-phenyl-4,6-diazatricyclo[6.4.0.0^{2,6}]*dodeca-1(12),8,10-trien-7-one* (**32**). After irradiation of (**31**) (0.006 mol) in benzene for 5 h, the residue was purified by silica-gel chromatography with chloroform as eluant, followed by recrystallization from ethyl acetate, to give one *diastereoisomer* of compound (**32**) in 26% yield, m.p. 175—177 °C; $\nu_{max.}$(Nujol) 3 275 and 1 695 cm^{-1}; $\delta_H(CDCl_3)$ 7.75 (1 H, s), 7.50 (5 H, s), 7.25 (5 H, s), 7.0 (1 H, s), 4.45 (1 H, d, *J* 6 Hz), 4.05 (1 H, d, *J* 6 Hz), 4.00 (1 H, d, *J* 12 Hz), 3.60 (1 H, reduced in D_2O), 3.50 (1 H, s), and 3.30 (1 H, d, *J* 12 Hz); $\delta_C(CDCl_3)$ 168.6, 144.3, 137.6, 136.5, 133.7, 129.1, 128.7, 128.6, 128.1, 127.7, 126.6, 126.1, 125.6, 93.5, 73.7, 64.8, and 56.3 p.p.m.; *m/z* 426 (M^+), 196, 118, and 91 (base) (Found: C, 64.7; H, 4.4; N, 6.6; Cl, 16.4. $C_{23}H_{18}Cl_2N_2O_2$ requires C, 64.94; H, 4.24; N, 6.59; Cl, 16.71%). The second diastereoisomer was obtained as *crystals* (3%) by h.p.l.c. (silica gel, 5μm spherisorb; chloroform–hexane), m.p. 173—175 °C; $\delta_H(CDCl_3)$ 7.70 (1 H, s), 7.20 (10 H, m), 6.60 (1 H, s), 4.80 (1 H, d, *J* 7 Hz), 4.10 (1 H, s), 3.85 (1 H, d, *J* 14 Hz), 3.70 (1 H, d, *J* 7 Hz), 3.40 (1 H, d, *J* 14 Hz), and 3.1 (1 H, br); $\delta_C(CDCl_3)$ 172.5, 137.5, 130.5, 128.9, 128.7, 128.4, 127.5, 126.3, 125.4, 98.5, 76.6, 64.7, and 55.4 p.p.m. (Found: C, 64.2; H, 4.55; N, 6.3%). A third product was also isolated by h.p.l.c. as crystals (3%), m.p. 62—63 °C; $\delta_H(CDCl_3)$ 7.40 (1 H, s), 7.10 (1 H, s), and 5.40 (1 H, s); $\delta_C(CDCl_3)$ 150.7, 132.2, 129.7, 128.5, 119.0, and 117.9 p.p.m.

4-Benzyl-2-hydroxy-3-phenyl-4,6,9(or 12)-triazatricyclo[6.4.0.0^{2,6}]*dodeca-1(12),8,10-trien-7-one* (**34**). After irradiation of (**33**) (0.009 mol) in benzene for 14 h, the residue was purified by silica-gel chromatography with chloroform–methanol as eluant. Only one fraction could be further purified by recrystallization from tetrachloromethane, to give crystals of *compound* (**34**) in 7% yield, m.p. 167—169 °C; $\nu_{max.}$(Nujol) 3 300, 1 690, and 1 670 cm^{-1}; $\delta_H(CDCl_3)$ 8.75 (1 H, dd, *J* 4 and 1.5 Hz), 8.10 (1 H, dd, *J* 6 and 1.5 Hz), 7.75—7.15 (11 H, m), 4.60 (1 H, d, *J* 7 Hz), 4.25 (1 H, d, *J* 7 Hz), 3.85 (1 H, d, *J* 12 Hz), 3.75 (1 H, s), 3.35 (1 H, d, *J* 12 Hz), and 3.30 (1 H, s, reduced in D_2O); $\delta_C(CDCl_3)$ 171.6, 153.7, 132.5, 129.6, 129.3, 129.0, 128.9, 128.6, 127.6, 124.8, 93.2, 72.8, 64.8, and 56.7 p.p.m. (Found: C, 74.0; H, 5.4; N, 11.8. $C_{22}H_{19}N_3O_2$ requires C, 73.95; H, 5.36; N, 11.76%).

4-Benzyl-2-hydroxy-3-phenyl-4,6,10(or 11)-triazatricyclo[6.4.0.0^{2,6}]*dodeca-1(12),8,10-trien-7-one* (**36**). After irradiation of (**35**) (0.008 mol) in benzene for 13 h, the residue was purified by silica-gel chromatography with chloroform–methanol as eluant. The mixture of isomers (53%) was separated by further silica-gel chromatography to give crude samples of the 10- and 11-aza compounds. ^1H N.m.r. analysis indicated that each was >80% pure; for the 11-aza compound (**36a**), $\delta_H(CDCl_3)$ 8.65 (1 H, d, *J* 5 Hz), 8.42 (1 H, s), 7.5—7.3 (6 H, m), 7.24 (5 H, s), 4.4 (1 H, br), 4.39 (1 H, d, *J* 6.5 Hz), 4.10 (1 H, d, *J* 6.5 Hz), 4.01 (1 H, d, *J* 11 Hz), 3.43 (1 H, s), and 3.25 (1 H, d, *J* 11 Hz); for the 10-aza compound (**36b**), $\delta_H(CDCl_3)$ 8.93 (1 H, s), 8.73 (1 H, d, *J* 5 Hz), 7.4 (5 H, m), 7.24 (5 H, s), 7.08 (1 H, d, *J* 5 Hz), 4.37 (1 H, d, *J* 6 Hz), 4.10 (1 H, d, *J* 6 Hz), 4.00 (1 H, d, *J* 11 Hz), 3.40 (1 H, s), and 3.24 (1 H, d, *J* 11 Hz).

4-Benzyl-2-hydroxy-3-phenyl-4,7-diazatricyclo[7.4.0.0^{2,7}]*trideca-1(13),9,11-trien-8-one* (**39**). The preparation of (**39**) and (**40**), and spectral data for (**40**), have already been reported.[5] For (**39**), $\nu_{max.}$(Nujol) 3 400 and 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 7.75—6.9 (14 H, m), 5.2 (1 H, br), 4.6—4.3 (2 H, m, including s at δ 4.39), and 3.7—2.4 [5 H, m, including 2 d (3.57 and 3.22), *J* 13 Hz]; $\delta_C(CDCl_3)$ 166.0, 143.5, 137.6, 132.7, 132.0, 129.7, 129.5, 128.9, 128.7, 128.2, 128.1, 127.7, 123.3, 122.2, 86.9, 69.6, 58.9, 43.3, and 35.6 p.p.m.; *m/z* 370 (M^+), 352, 279, and 91 (base) (Found: C, 77.8; H, 6.1; N, 7.3. $C_{24}H_{22}N_2O_2$ requires C, 77.80; H, 6.00; N, 7.56%).

Table 1. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	−0.175 9(1)	0.221 5(1)	0.179 77(5)
O(2)	0.205 0(2)	0.333 8(1)	0.250 69(6)
N(1)	0.046 0(2)	0.243 8(1)	0.209 50(6)
N(2)	0.137 8(2)	0.177 2(1)	0.141 38(5)
C(1)	0.105 6(2)	0.328 5(1)	0.224 76(6)
C(2)	0.030 3(2)	0.409 6(1)	0.203 77(7)
C(3)	0.039 0(2)	0.508 5(1)	0.213 70(8)
C(4)	−0.044 3(2)	0.569 9(1)	0.187 41(9)
C(5)	−0.132 5(2)	0.533 2(2)	0.153 48(9)
C(6)	−0.141 4(2)	0.434 3(2)	0.143 67(8)
C(7)	−0.057 6(2)	0.373 1(1)	0.169 60(6)
C(8)	−0.051 9(2)	0.263 2(1)	0.170 00(7)
C(9)	0.005 8(2)	0.206 8(1)	0.124 80(7)
C(10)	0.126 0(2)	0.161 1(1)	0.194 67(7)
C(11)	0.196 1(2)	0.095 7(1)	0.113 71(7)
C(12)	0.118 2(2)	0.002 0(1)	0.112 75(7)
C(13)	0.126 5(2)	−0.064 4(1)	0.151 38(8)
C(14)	0.055 2(3)	−0.149 9(2)	0.150 2(1)
C(15)	−0.024 9(3)	−0.170 9(2)	0.110 6(1)
C(16)	−0.035 2(3)	−0.106 2(2)	0.071 8(1)
C(17)	0.036 6(3)	−0.019 9(2)	0.073 05(8)
C(18)	0.009 0(3)	0.262 8(1)	0.076 92(6)
C(19)	0.111 1(2)	0.326 4(1)	0.066 10(7)
C(20)	0.109 3(3)	0.379 2(2)	0.022 57(9)
C(21)	0.005 0(4)	0.368 0(2)	−0.010 42(9)
C(22)	−0.095 0(3)	0.304 3(2)	0.000 4(1)
C(23)	−0.093 5(2)	0.251 4(2)	0.043 59(9)
H(1)	−0.2169	0.2585	0.2073
H(2)	0.1053	0.5346	0.2388
H(3)	−0.0404	0.6423	0.1946
H(4)	−0.1927	0.5808	0.1347
H(5)	−0.2060	0.4074	0.1181
H(6)	−0.0495	0.1483	0.1157
H(7)	0.2152	0.1599	0.2117
H(8)	0.0804	0.0971	0.2026
H(9)	0.2861	0.0807	0.1288
H(10)	0.2112	0.1170	0.0786
H(11)	0.1861	−0.0487	0.1812
H(12)	0.0604	−0.1983	0.1786
H(13)	−0.0786	−0.2333	0.1101
H(14)	−0.0922	−0.1221	0.0418
H(15)	0.0275	0.0287	0.0444
H(16)	0.1877	0.3345	0.0901
H(17)	0.1852	0.4271	0.0154
H(18)	0.0041	0.4079	−0.0423
H(19)	−0.1691	0.2952	−0.0248
H(20)	−0.1688	0.2037	0.0517

Phosphorescence Studies.—Measurements were made using a Perkin-Elmer MPF4 instrument with Hitachi S10 photomultiplier. The spectra were fully corrected, and the 0—0 bands were assigned by curve-fitting averaged over a number of runs.

Structure Determination of Compound (**37**) *by X-Ray Diffraction.*—Crystals of (**37**) were grown as clear prisms. Diffraction intensities were collected from a crystal of dimensions 0.50 × 0.25 × 0.20 mm on a CAD-4 four-circle diffractometer. Of the total 3 863 reflections (complete for $2\theta \leqslant 74°$), 2 885 satisfied the criterion $I \geqslant 3\sigma(I)$, and only these were used in the solution and refinement of the structure.

Crystal Data.—$C_{23}H_{20}N_2O_2$, *M* = 356.4, orthorhombic, *a* = 10.1082(5), *b* = 13.7636(10), *c* = 27.0813(12) Å, *U* =

Table 2. Bond distances (Å) and bond angles (°)

(*a*) Distances

C(1)–O(2)	1.228(2)	N(2)–C(11)	1.471(2)
C(1)–C(2)	1.466(3)	C(11)–C(12)	1.512(3)
C(2)–C(7)	1.378(2)	C(12)–C(13)	1.391(3)
C(7)–C(8)	1.513(2)	C(13)–C(14)	1.381(3)
C(8)–N(1)	1.481(2)	C(14)–C(15)	1.373(4)
C(1)–N(1)	1.376(2)	C(15)–C(16)	1.382(4)
C(2)–C(3)	1.390(2)	C(16)–C(17)	1.392(4)
C(3)–C(4)	1.390(3)	C(17)–C(12)	1.388(3)
C(4)–C(5)	1.376(3)	C(9)–C(18)	1.508(2)
C(5)–C(6)	1.390(3)	C(18)–C(19)	1.385(3)
C(6)–C(7)	1.386(3)	C(19)–C(20)	1.385(3)
C(8)–O(1)	1.404(2)	C(20)–C(21)	1.390(4)
C(8)–C(9)	1.562(2)	C(21)–C(22)	1.370(5)
C(9)–N(2)	1.466(2)	C(22)–C(23)	1.379(4)
N(2)–C(10)	1.464(2)	C(23)–C(18)	1.383(3)
C(10)–N(1)	1.454(2)		

(*b*) Angles

O(2)–C(1)–N(1)	125.5(2)	C(10)–N(2)–C(11)	114.8(1)
C(2)–C(1)–N(1)	107.5(2)	C(10)–N(2)–C(9)	105.7(1)
C(2)–C(1)–O(2)	127.0(2)	C(9)–N(2)–C(11)	114.9(2)
C(3)–C(2)–C(7)	121.9(2)	N(2)–C(11)–C(12)	116.7(2)
C(3)–C(2)–C(1)	129.6(2)	C(11)–C(12)–C(13)	121.1(2)
C(1)–C(2)–C(7)	108.5(2)	C(11)–C(12)–C(17)	120.6(2)
C(2)–C(7)–C(8)	109.6(2)	C(13)–C(12)–C(17)	118.4(2)
C(2)–C(7)–C(6)	120.8(2)	C(12)–C(13)–C(14)	120.7(2)
C(6)–C(7)–C(8)	129.4(2)	C(13)–C(14)–C(15)	120.3(2)
N(1)–C(8)–C(9)	103.1(1)	C(14)–C(15)–C(16)	120.2(2)
N(1)–C(8)–C(7)	102.2(1)	C(15)–C(16)–C(17)	119.4(3)
N(1)–C(8)–O(1)	112.7(2)	C(12)–C(17)–C(16)	120.9(2)
C(7)–C(8)–O(1)	112.1(2)	N(2)–C(9)–C(8)	103.8(1)
C(9)–C(8)–O(1)	106.1(1)	N(2)–C(9)–C(18)	112.7(2)
C(7)–C(8)–C(9)	120.3(2)	C(8)–C(9)–C(18)	115.4(1)
C(1)–N(1)–C(10)	120.2(2)	C(9)–C(18)–C(19)	121.4(2)
C(1)–N(1)–C(8)	110.9(1)	C(9)–C(18)–C(23)	119.1(2)
C(8)–N(1)–C(10)	108.2(1)	C(19)–C(18)–C(23)	119.5(2)
C(2)–C(3)–C(4)	117.3(2)	C(18)–C(19)–C(20)	120.1(2)
C(3)–C(4)–C(5)	120.8(2)	C(19)–C(20)–C(21)	119.9(3)
C(4)–C(5)–C(6)	121.9(2)	C(20)–C(21)–C(22)	119.6(2)
C(5)–C(6)–C(7)	117.3(2)	C(21)–C(22)–C(23)	120.7(3)
N(1)–C(10)–N(2)	101.5(1)	C(22)–C(23)–C(18)	120.2(3)

3 767.69 Å^3, $Z = 8$, $D_c = 1.26$ g cm^{-3}, $F(000) = 1\,504$, space group *Pbca*, Cu-K_α *X* radiation (graphite monochromator), $\lambda = 1.5418$ Å.

Structure Solution and Refinement.—The structure was solved using direct methods and, in the final refinement by full-matrix least-squares, anisotropic thermal parameters were used for all non-hydrogen atoms. All calculations were performed on the Cambridge IBM 370 computer using the SHELX package of programs. Hydrogen atoms were incorporated at calculated positions, but neither their positional nor thermal (U 0.05) parameters were refined. The refinement converged to R 0.042 with a mean shift-to-error ratio in the last cycle of 0.001. The data were not corrected for the efffects of *X*-ray absorption. Atomic scattering factors were taken from reference 23 for hydrogen and from reference 24 for all other atoms. Positional parameters are shown in Table 1, bond lengths and angles in Table 2. Thermal parameters for non-hydrogen atoms are listed in Supplementary Publication No. SUP 56102 (2 pp.).

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