Factors affecting the Electronic States of Amidyls: Evidence for Π—Σ Mixing in Simple Amidyls

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N-Methyl- and *N*-acetyl-biphenyl-2-carboxamidyls, generated from the corresponding *N*-bromides in photochemically initiated alkyl radical or bromine atom chain reactions, cyclise to give Ar_1-5 and Ar_2-6 products, indicating the accessibility of a low-energy excited Σ-state for these species. *N*-Methoxybiphenyl-2-carboxamidyl radical, from photolysis of the *N*-chloro derivative, yields no products from Ar_1-5 or Ar_2-6 cyclisation; this indicates a thermodynamically stable Π-ground state and a high-energy and thermally inaccessible excited Σ-state. The *N*-methylbiphenyl-2-sulphonamidyl radical from photolysis of the *N*-iodo or *N*-bromo derivative affords only the Ar_2-6 product; this represents chemical evidence for a large Π—Σ energy separation. MNDO calculations predict the Π-ground states of *N*-alkoxy-amidyls and -aminyls to be more nucleophilic than those of amidyls, imidyls, and sulphonamidyls, in keeping with the observed reactivities. The reactivities and regioselectivities observed, together with e.s.r. data and MNDO results, support mixing between the Π-ground and Σ-excited states of amidyls, whereas alkoxyamidyls, cyclic amidyls, and sulphonamidyls have pure Π-ground states. Mixing in amidyls is facilitated by their acyclic nature and by a small energy difference between their Π-ground and Σ-excited states.

Amidyl (**1**), imidyl (**2**), and sulphonamidyl (**3**) radicals belong to a class which, because of the non-bonding electrons, can have two distinct electronic states where the electron resides upon the singly bonded heteroatom. For amidyls these states are designated Π (**4**) and Σ (**5**).

Much physical (e.s.r.)[1-7] and theoretical (MO)[2,8-11] evidence points to a Π-ground state for amidyls (**1**). Calculations point to a Π-ground state of imidyls (**2**).[11-13] Both e.s.r.[6,14-16] and *ab initio* calculations[10] point to a Π-ground state for sulphonamidyls.

The search for chemical evidence for the ground state structures of (**1**) and (**2**) has revealed interesting results. Skell and his co-workers[17] have suggested that both Σ- and Π-states of the succinimidyl radical can be generated selectively from *N*-bromosuccinimide in chain reactions involving, respectively, nucleophilic primary or secondary alkyl radicals and electrophilic halogen atoms in abstraction of the *N*-bromine atom. Although these routes have been supported by MNDO calculations,[13] recent papers by Tanner[18] and by Walling[19] have questioned the intermediacy of different radical states in chain bromination. *Ab initio* calculations[12] show that the Σ-state is higher in energy than the Π-state by 84—105 kJ mol^{-1}; MNDO provides a difference of 61 kJ mol^{-1}.[11]

The participation of the Σ-state (**5**) of the biphenyl-2-carboxamidyl radical (**11**), formed by photolysis of the *N*-iodamide (**6**), is indicated by the formation of Ar_1-5 cyclised products (**14**)—(**16**).[20-22] Although the intermediate radical (**25**) is thermodynamically less stable than (**27**), the Ar_1-5 mode of addition is irreversible at temperatures below 333 K.[23] This mode is peculiar to the Σ-state since in the transition state (**28**) there is optimum orbital overlap between nitrogen and the C-1′.

Not only would the Π-state radical present an orthogonal orbital to the same carbon atom (**29**), but its involvement would require an increase in potential energy due to repulsion between the *N*-substituent and the *o*-phenyl ring, as well as a loss in conjugation of the radical with the carbonyl group, both as a consequence of the twisting required to effect reasonable overlap. After bond formation, there would of necessity be a rehybridisation at nitrogen to give an in-plane *N*-alkyl substituent. These unfavourable effects would oppose the least-motion principle,[24] but would be circumvented if electronic reorganisation to the Σ-state (at relatively small cost and resulting in better overlap) were to take place. Furthermore, as in thermal homolytic cleavage of *N*-halogenoamides or diacylhydrazines,[25] symmetry dictates that the ring opening of the spirocyclohexadienyl radical (**25**) would correlate with the Σ-state of the amidyl, which, by the principle of microscopic reversibility, would also be expected to participate in the formation of (**25**). The Σ-state or the Π-ground state may be responsible for Ar_2-6 product formation.* Similar arguments pertain to the implication of the Σ-state in intramolecular olefin addition reactions.[26] Selectivities in intramolecular hydrogen abstraction reactions point to the Π-ground state amidyl being the radical responsible.[7,27] These results indicate that while amidyls have a Π-ground state, it is conceivable that the Σ-state which is close in energy is thermally accessible, and participates when reaction from the Π-ground state suffers from unfavourable enthalpy or entropy effects in the transition state.[28] In such instances the energy separation between the Π- and Σ-states forms a component of the overall activation energy (E_A) for the reaction. The E_A for Ar_1-5 cyclisation of *N*-methylbiphenyl-2-carboxamidyl radicals of 63 kJ mol^{-1} [21] thus sets an upper bound for the energy separation in (**11**). Recent *ab initio* calculations predict the energy separation of simple amidyls to be only 20 (STO-3G), 28 (4-31G),[9] or 19.7 kJ mol^{-1},[10] allowing mixing of the two states, although the MNDO value is much greater (63 kJ mol^{-1}).[11] In contrast sulphonamidyls (**3**) should exhibit a larger energy separation since at *ab initio* level the difference is 100 kJ mol.[10]

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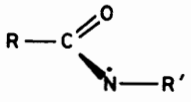
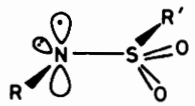
‡ We originally proposed that the Π-state amidyl led to Ar_2-6 cyclisation, since only substrates with full conjugation between the N and the site of addition undergo cyclisation.[21] While this appears to be the case for acyloxyl radical cyclisations,[28] we cannot rule out the participation of Σ-state in the case of amidyls.



(1) R' = H or alkyl

(2) R' = acyl



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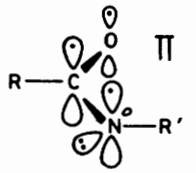

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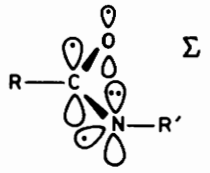

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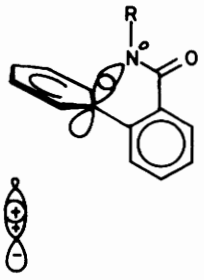

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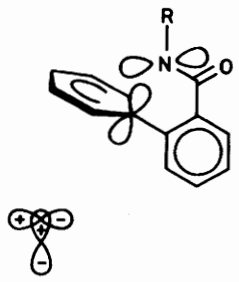

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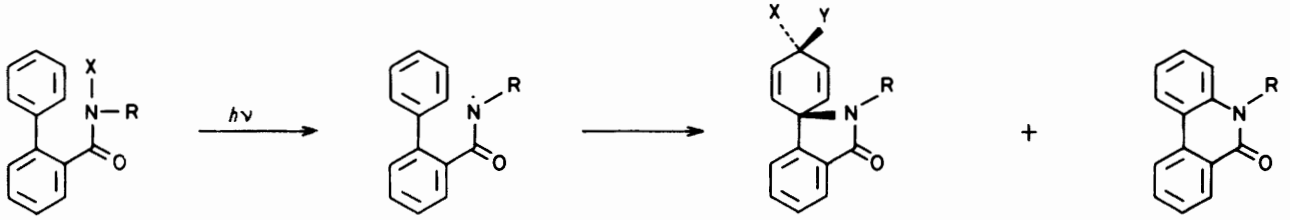
Results

(a) N-*Bromo*-N-*methylbiphenyl*-2-*carboxamide* (7).—Photolysis (>300 nm) of *N*-bromo-*N*-methylbiphenyl-2-carboxamide (7), in the presence of an excess of the bromine atom scavenger 3,3-dimethylbut-1-ene,[17] gave a mixture which, from integration of the n.m.r. *N*-methyl signals, consisted of parent



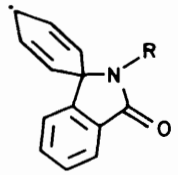
(6) R = Me, X = I
(7) R = Me, X = Br
(8) R = Ac, X = Br
(9) R = OMe, X = Br, I
(10) R = OMe, X = Cl

(11) R = Me
(12) R = Ac
(13) R = OMe

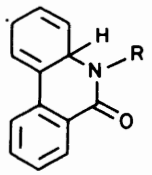
(14) R = Me, X = Bu^{t}O, Y = H
(15) R = Me, X = H, Y = Bu^{t}O
(16) R = Me, XY = O
(17) R = Me, X = Br, Y = H
(18) R = Me, X = H, Y = Br
(19) R = Me, X = AcO, Y = H
(20) R = Me, X = H, Y = AcO
(21) R = Ac, X = Br, Y = H

(22) R = Me
(23) R = Ac
(24) R = OMe

Scheme 1.



(25) R = CH_3
(26) R = Ac



(27) R = CH_3

In order to substantiate the participation of the Σ-state in Ar_1-5 cyclisation, as well as to elaborate upon factors affecting the relative energies of Σ- and Π-states of amidyl radicals, we have studied further the reactions of *N*-methylbiphenyl-2-carboxamidyl, and have also studied *N*-acetyl- and *N*-methoxybiphenyl-2-carboxamidyls as well as *N*-methylbiphenyl-2-sulphonamidyl.

In addition we have investigated the effect of bromine chain inhibition, in order to establish whether selective Σ- or Π-state formation could be initiated according to the theories of Clark[13] and as alluded to by Skell[17] *et al.* for succinimidyl radicals.

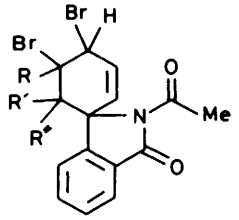
amide (32%), the Ar_2-6 product *N*-methylphenanthridone (**22**) (20%), the epimeric Ar_1-5 products 4′-bromo-2-methyl-3-oxoisoindoline-1-spiro-1′-cyclohexa-2′,5′-dienes (**17**) and (**18**) (45%), and 1,2-dibromo-3,3-dimethylbutane (Scheme 1). A mixture of the spirocyclohexadienyl bromides (**17**) and (**18**) was isolated by preparative h.p.l.c. The major component was isolated by fractional crystallisation and was assigned the *trans*-configuration (**17**) since its *N*-methyl resonance in the ^{1}H n.m.r. spectrum was 0.1 p.p.m. to high field of that of (**18**). A similar relationship has been reported for the *N*-methyl resonances of the corresponding acetates (**19**) and (**20**),[29] the structures of which were confirmed by *X*-ray analysis of the alcohol derived from (**19**).[30] The phenanthridone (**22**) would arise from the reaction of (**27**) with a source of bromine, followed by a loss of HBr.

Photolysis of (**7**) in the absence of 3,3-dimethylbutene afforded a similar ratio of products (Table), although the reaction proceeded more rapidly, indicating the participation of bromine atom chains.

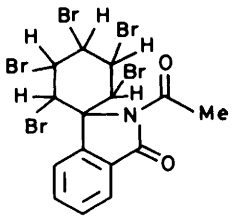
(b) N-*Acetyl*-N-*bromobiphenyl*-2-*carboxamide* (**8**).—Similar results were obtained upon photolysis of *N*-acetyl-*N*-bromobiphenyl-2-carboxamide (**8**). U.v. irradiation (>300 nm) of a

Table. Ratios Ar_2-6:Ar_1-5 for the photolysis of (7) in benzene at room temperature

	Ar_2-6:Ar_1-5	
	Bromine	No Bromine (3,3-dimethylbutene)
Expt. 1	0.31	0.27
Expt. 2	0.30	0.23



(30) R = H, R′ = R* = Br
(31) R = R′ = Br, R* = H
(32) R = R′ = H, R* = Br



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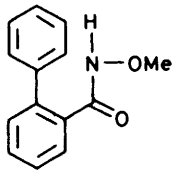

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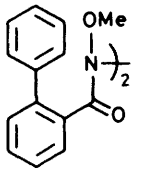

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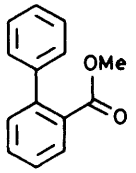
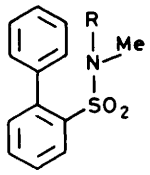


(36)

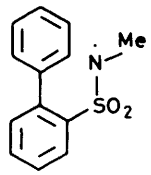
benzene solution of (**8**) containing 3,3-dimethylbutene gave a mixture containing the parent *N*-acetyl amide (50%), *N*-acetylphenanthridone (**23**) (31%), and 2-acetyl-4′-bromo-3-oxoisoindoline-1-spiro-1′-cyclohexa-2′,5′-diene (**21**) (31%), which was isolated nearly pure by repetitive preparative h.p.l.c. and characterised spectroscopically. The *trans*-configuration in (**21**) is assigned on steric grounds. In the absence of bromine scavenger, photolysis of (**8**) afforded a mixture of *N*-acetylphenanthridone (**23**) and several other components which could not be separated. The formation of Ar_1-5 products was established unequivocally from a similar photolysis of (**8**) in benzene to which 2 equiv. of bromine were added. Apart from *N*-acetylphenanthridone (**23**), five γ-lactam components were isolated, whose properties were consistent with polybrominated adducts of (**21**). Microanalytical results and n.m.r. and mass spectroscopy permitted the identification of four of these as (**30**)—(**33**).

(c) N-*Halogeno*-N-*methoxybiphenyl*-2-*carboxamides*.—Treatment of the amide (**34**) with an excess of t-butyl hypoiodite in t-butyl alcohol or t-butyl hypobromite in benzene in the dark afforded, instead of the *N*-iodo- or *N*-bromo-amide (**9**), *N*-methoxyphenanthridone (**24**), *N*,*N*′-dimethoxy-*N*,*N*′-bis(biphenyl-2-ylcarbonyl)hydrazine (**35**), and methyl biphenyl-2-carboxylate (**36**) in reactions which we have ascribed to heterolytic processes involving intermediate *N*-alkoxy-*N*-acylnitrenium ions.[31]

N-Chloro-*N*-methoxybiphenyl-2-carboxamide (**10**) could be obtained by the reaction of (**34**) with t-butyl hypochlorite in benzene. Photolysis of (**10**) at room temperature in dry benzene and in the presence of 3,3-dimethylbutene as chlorine atom



(37) R = H
(38) R = I
(39) R = Br



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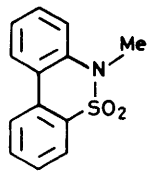


(41)

scavenger gave only the dimer (**35**) (33%) and its decomposition product, the ester (**36**) (35%). No *N*-methoxyphenanthridone could be detected by n.m.r. or h.p.l.c.[31] The intermediacy of the radical (**13**) was proved by repeating the photolysis in the presence of the radical quencher 2,6-di-t-butyl-4-methylphenol, whereupon only the amide (**34**) was recovered. The quencher reacted very slowly with the *N*-chloro-*N*-methoxyamide under these conditions.

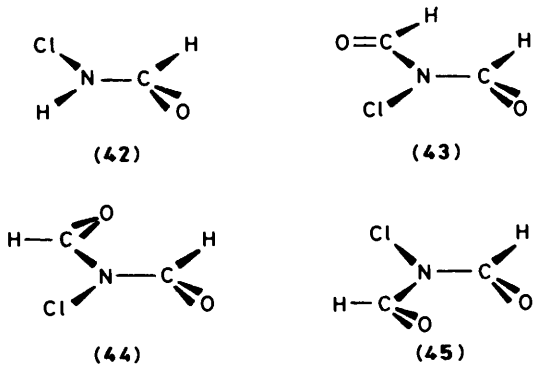
(d) N-*Halogenobiphenyl*-2-*sulphonamides*.—*N*-Methylbiphenyl-2-sulphonamidyl radical (**40**) was generated by photolysis of the *N*-iodosulphonamide (**38**) (formed in t-butyl alcohol with t-butyl hypoiodite) or of the *N*-bromosulphonamide (**39**) in benzene. These conditions facilitate interception of spirocyclohexadienyl radical intermediates in the analogous photolysis of *N*-halogenoamides[20–22] and acyl hypoiodites.[28] However, irradiation of (**38**) in t-butyl alcohol for 4 h at room temperature afforded, after reductive work-up and chromatographic separation, only the sultam (**41**) (21%) and unchanged sulphonamide (**37**). The n.m.r. spectrum of the crude reaction mixture was devoid of resonances indicative of Ar_1-5 cyclisation products. The *N*-methyl singlet of (**41**) (τ 6.6) and *N*-methyl doublet of the sulphonamide (**37**) (τ 7.69) were both *ca.* 0.3 p.p.m. upfield of the analogous signals of *N*-methylphenanthridone (**22**) (τ 6.33) and *N*-methylbiphenyl-2-carboxamide (τ 7.32), and γ-sultam *N*-methyl singlets likewise would be expected to resonate 0.3 p.p.m. upfield of γ-lactam *N*-methyl singlets (τ 7.0—7.1). A dark reaction for the same time afforded unchanged sulphonamide (**37**).

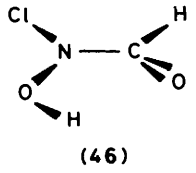
N-Bromobiphenyl-2-sulphonamide (**39**) was isolated from (**37**) and t-butyl hypobromite in benzene. Photolysis of (**39**) in benzene under nitrogen, both in the presence and in the absence of 3, 3-dimethylbutene, gave good conversions into the sultam (**41**) (50% yield), with no evidence of the formation of Ar_1-5 cyclisation products.

Discussion

(a) N-*Methyl- and* N-*Acetyl-biphenyl*-2-*carboxamidyl Reactions; the Effect of Different Chain Carriers*.—MNDO calculations were carried out with geometry optimisation for the models *N*-chloroformamide (**42**), the three planar conformations of the acyclic *N*-chloroformimide (**43**)—(**45**), and *N*-hydroxyformamide (**46**). All substrates were predicted to have molecular orbital properties similar to those calculated by MNDO for *N*-chlorosuccinimide,[13] *viz.* that the HOMO and LUMO of these molecules have similar energies and have π* and σ* character respectively (Figure 1).

These results and those of Clark [13] are in accord with the e.s.r. results of Neilson and Symons,[32] who showed that the radical anions of *N*-chloro-, *N*-bromo-, and *N*-iodo-succinimide and *N*-bromoacetamide have σ* character. Accordingly it was envisaged that the reaction of the *N*-bromo derivatives of *N*-methyl-, *N*-acetyl-, or *N*-methoxy-biphenyl-2-carboxamide with bromine atoms or alkyl radicals could give their Π- and Σ-states respectively. It was expected that if amidyls could





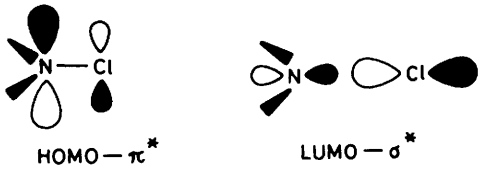


Figure 1. Typical frontier orbitals of *N*-chloroformamides (**42**)—(**46**)

be generated under Σ-radical conditions (bromine atom scavenging[17]) Ar_1-5 products would be formed, while conditions leading to the Π-ground state (bromine atom chains[17]) should lead either to no cyclisation products if this state is too stable to interact with the *o*-phenyl substituent, or to Ar_2-6 products only.

The nature and yields of products from irradiation of the *N*-bromo-*N*-methylamide (**7**) were essentially invariant, both in the presence and in the absence of 3,3-dimethylbutene. Furthermore, the spiro-cyclised products (**21**) and (**30**)—(**33**) were formed in similar yields from irradiation of the *N*-bromo-*N*-acetyl amide (**8**) in the presence of bromine. We therefore conclude that the different radical generation conditions either lead to formation of the same radical state or if different states are formed initially there must be a rapid electronic rearrangement to a common and lower energy state from which reaction occurs. In support of this, photochemical cleavage of *N*-halogenoamides must involve n–σ^* excitation,[32] which, like thermal cleavage, should lead to formation of the Σ-state of the radical. However, e.s.r. spectra of photochemically generated amidyl radicals always indicate a Π-state for the radical[1–7] indicating rapid relaxation to the Π-ground state. On the basis that Ar_1-5 cyclised products are derived from the higher energy Σ-state amidyl, this state must be thermally accessible from the Π-state by state mixing, a process which would be facilitated if the states are closed in energy.[9,10]

Theoretical[11,12] and experimental[17e] estimations give a large difference in energy between the Σ- and Π-states in planar imidyls which should inhibit state mixing (the difference is three to five times larger than that for amidyls at *ab initio* level). However, the strong steric interactions in the biphenyl substrate might conceivably cause the *N*-acetyl group in (**12**) to be twisted

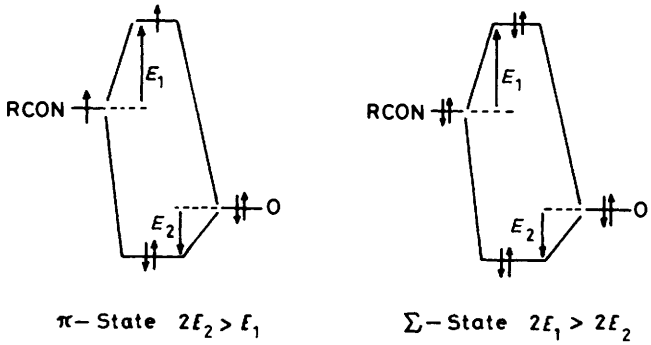


Figure 2. Molecular orbital energies for alkoxyamidyls

out of the amide plane, leading to radical properties similar to those of the *N*-methylamidyl (**11**). The formation of one spirocyclised bromide (**21**) from (**8**) as opposed to two (**17**) and (**18**) from the methyl amide (**7**) is consistent with greater bulkiness of the *N*-acetyl group, which apparently completely inhibits bromine transfer to the β-face of the spirocyclohexadienyl radical intermediate (**26**).

(b) N-*Methoxybiphenyl-2-carboxamidyl Reactions.*—The formation of the dimer (**35**) from irradiation of *N*-chloro-*N*-methoxybiphenyl-2-carboxamide is consistent with the reactions of other alkoxy amidyls.[2,14,33] However, Forrester *et al.* have reported competitive intramolecular cyclisation of *N*-methoxybiphenyl-2-carboxamidyl (**13**) to *N*-methoxyphenanthridone (**24**) in 20% yield upon oxidation of *N*-methoxybiphenyl-2-carboxamide (**34**) with aqueous persulphate at 100 °C.[14] In an effort to effect intramolecular reactions, the *N*-chloroamide (**10**) was irradiated in an adamantane matrix. The reaction gave the methoxyamide (**34**) and methyl biphenyl-2-carboxylate (**36**), but no *N*-methoxyphenanthridone (**24**) could be detected by n.m.r. or h.p.l.c. The possibility that persistent radicals, trapped in the matrix, reacted bimolecularly upon dilution to give the dimer (**35**), which decomposed to the ester (**36**), was eliminated by dissolving the matrix after irradiation in a benzene solution of 2,6-di-t-butyl-4-methylphenol. The products were still amide and ester. The mechanism by which (**36**) is formed in the adamantane matrix has not yet been resolved. As expected, photolysis of *N*-bromo-*N*-methylbiphenyl-2-carboxamide (**7**) in an adamantane matrix afforded similar yields of Ar_1-5 and Ar_2-6 cyclised products to those obtained from solution photolysis.

E.s.r. evidence indicates a Π-ground state for alkoxyamidyls (**4**; R′ = OMe) with spin delocalisation onto oxygen.[2,14,34] The tendency of (**13**) to dimerise in solution reflects this greater thermodynamic stability. In valence bond terms the Π-state of alkoxyamidyls is stabilised by resonance [(**47**) ⟷ (**48**)] which

$$\underset{(47)}{R\text{–}C(O)\text{–}\dot{N}\text{–}\ddot{O}R'} \longleftrightarrow \underset{(48)}{R\text{–}C(O)\text{–}\overset{-}{\ddot{N}}\text{–}\overset{+}{\dot{O}}\text{–}R}$$

must render it lower in energy than the Π-state of amidyls or imidyls. In molecular orbital parlance this stabilisation arises owing to a net excess of Π-bonding character over Π-antibonding character as a consequence of double occupancy of the lower energy Π orbital and single occupancy of the upper Π* orbital (Figure 2).

Furthermore the Π-ground state of the alkoxyamidyl (**13**) should be less electrophilic than that of the methylamidyl (**11**) or the acetylamidyl (**12**), since the SOMO of (**13**) should be higher than the SOMO of (**11**) or (**12**).[35] This is supported by MNDO calculations on the ground states of the model aminyl

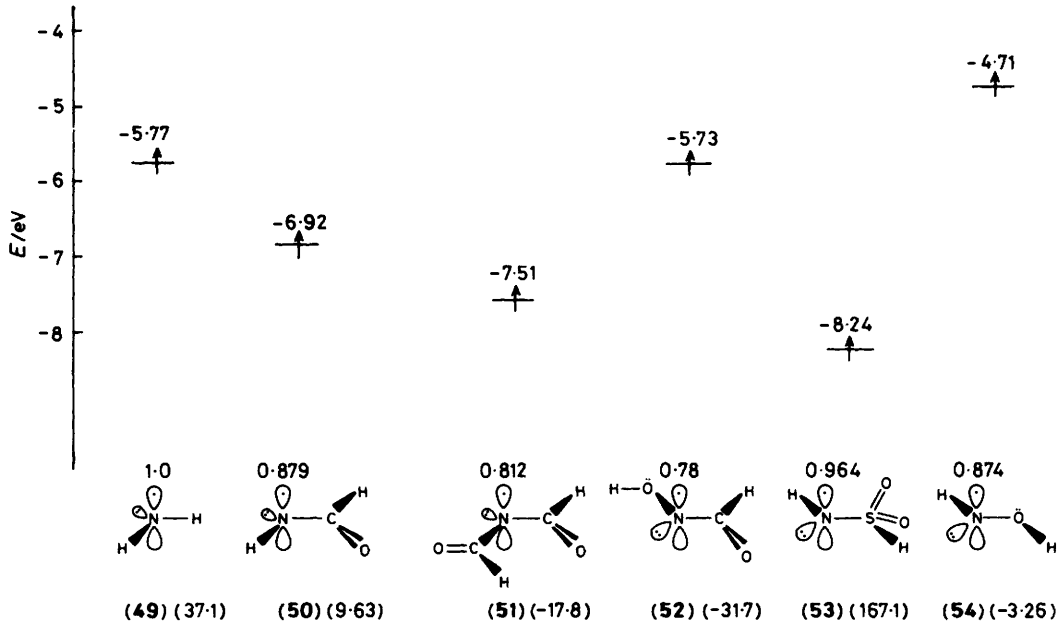


Figure 3. SOMO energies, $2p_z$ coefficients, and ΔH_f values (in parentheses) for nitrogen-centred free radicals

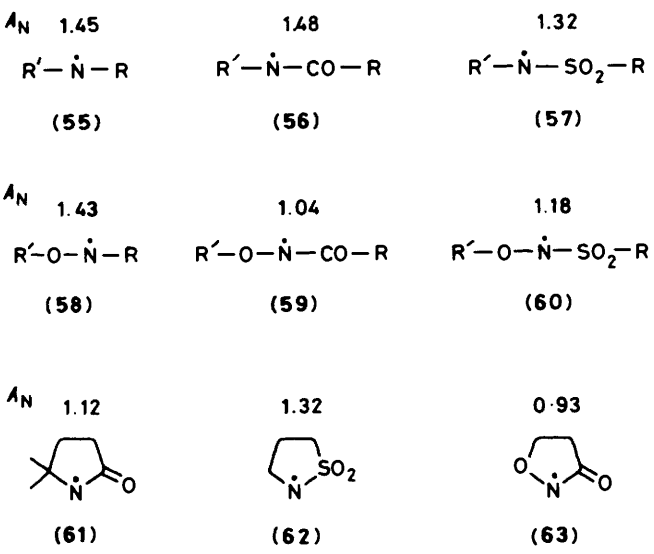


Figure 4. Typical A_N values (mT) for nitrogen free radicals

(**49**), formamidyl (**50**), *N*-formylformamidyl (**51**), and *N*-hydroxyformamidyl (**52**). All four radicals have a Π-ground state with optimised conformations, *N*-$2p_z$ coefficients, SOMO energies, and heats of formation shown in Figure 3. *N*-Hydroxyformamidyl (**52**) has a much lower ΔH of formation than (**49**), (**50**), or (**51**). The SOMO energies of ground state hydroxyamidyl (**52**) and aminyl (**49**) are similar and much higher than those of amidyl (**50**) and imidyl (**51**), and the reactions of alkoxyamidyls should resemble those of aminyl radicals which have no propensity to add to arenes and a low reactivity towards olefins.[36] Aminyls and alkoxyamidyls should also have a lower oxidation potential, and we have recently shown that, like *N*-chloroamines,[37] *N*-chloro-*N*-alkoxyamides readily react with Lewis acids to form nitrenium ions.[31]

The failure of (**13**) to produce Ar_1-5 cyclised products suggests that the Σ-state is much higher in energy than the Π-state and thus not accessible by thermal excitation. Qualitative molecular orbital arguments support this proposal. The Σ-state of alkoxyamidyls should be destabilised relative to that of amidyls since Π-antibonding character will be greater than Π-bonding character (Figure 2). These arguments imply that alkoxy, amino, or thio substituents should increase the Σ—Π energy separation relative to that for amidyls.

(c) *Reactions of* N-*Methylbiphenyl-2-sulphonamidyl Radicals.*—MNDO calculations on the model sulphonamidyl (**53**) predict a Π-ground state which is even more electrophilic than that for amidyls or imidyls (lower energy SOMO; Figure 3).* *Ab initio* calculations predict a large energy difference between the Π-ground and excited Σ-state for *N*-methylmethanesulphonamidyl (3; R = R′ = Me).[10] The formation of the δ-sultam (**41**) and the total absence of Ar_1-5 (γ-sultam) products are in concurrence with these theoretical arguments. Since γ-sultams are as readily formed as γ-lactams[15b,16] it is unlikely that the preponderence of δ-sultam is due to reversible Ar_1-5 cyclisation under these favourable trapping conditions.

Furthermore, δ-sultam formation adds credence to our proposal[21] that pure Π-state amidyls may undergo Ar_2-6 cyclisation. A similar preference for Ar_2-6 cyclisation has been noted for biphenyl-2-carboxyl radicals.[28]

E.s.r. Evidence for Mixing of Π- *and* Σ-*States in Amidyls.*—In recent years much e.s.r. data has become available on nitrogen free radicals. The relative magnitudes of coupling constants are at first confusing. Typical A_N values for a series of relevant radicals are given in Figure 4.

* MNDO is apparently not suited to calculations upon sulphur or phosphorus in their expanded valence states and such calculations must be treated with caution.[38] However, we have performed calculations upon phosphoramides and their derivatives with some success.[39] Furthermore, while ΔH_f of (**53**) is clearly too positive, the optimised geometry is close to that derived from *ab initio* calculations upon *N*-methylmethanesulphonamidyl (3; R = R′ = Me).[10]

Several points of discrepancy are apparent.

(i) Values of A_N for sulphonamidyls (**57**) are less than for amidyls (**56**) by 0.16 mT, despite the greater nitrogen localisation in the former radical.[6,10,14,15]

(ii) The difference in A_N values between the cyclic amidyl (**61**) and amidyls (**56**) (0.36 mT) is much greater than the corresponding difference between the cyclic oxyamidyl (**63**) and alkoxyamidyls (**59**) (0.11 mT), or between the cyclic sulphonamidyl (**62**) and sulphonamidyls (**57**) (*ca.* 0 mT).

(iii) The A_N decrease upon oxygen substitution in amidyls (**56**) ⟶ (**59**) is much greater (0.44 mT) than the corresponding decreases for sulphonamidyls (**57**) ⟶ (**60**) (0.14 mT), cyclic amidyls (**61**) ⟶ (**63**) (0.19 mT), and aminyls (**55**) ⟶ (**58**) (0.02 mT).

Although structural changes at nitrogen from one amidyl radical to another could lead to differences in A_N values, studies by Ingold,[3,4] Danen and Engberts,[15d] and their co-workers have shown that the configuration at the nitrogen atoms in acyclic and cyclic amidyls and in sulphonamidyls is essentially planar. The large variations in A_N values are, therefore, unlikely to be due to bending at nitrogen.

We contend that these discrepancies are explicable if it is assumed that A_N for amidyls is higher than expected owing to mixing in of the upper energy Σ-state. Furthermore, mixing between states is only possible if the radicals are acyclic and have a low-energy Σ-state. Engberts and his co-workers have used similar arguments to explain the difference outlined in (i) based on *ab initio* calculations on amidyl and sulphonamidyl.[10,15c,d] The similarity in A_N values for aminyls (**55**) and alkoxyaminyls (**58**) indicates that different π–σ spin polarisations operate in the species and different Q values must apply.[40] From MNDO N-$2p_z$ coefficients (Figure 3) for aminyl (**49**) and hydroxyaminyl (**54**), Q values of 1.45 and 1.87 mT are required for N̈ and O–N̈ radicals, respectively. From these values, the predicted A_N values for amidyl (**56**), alkoxyamidyl (**59**), and sulphonamidyl (**57**) based upon calculated N-$2p_z$ coefficients for (**50**), (**52**), and (**53**) are 1.12,* 1.13, and 1.35 mT. The correlation with experimental A_N values is excellent for sulphonamidyls (**57**), and the amidyl value fits the planar cyclic amidyl (**61**) exactly. The MNDO-optimised geometry for formamidyl (**50**) is also planar and the SOMO properties are probably a good reflection of those in (**61**). Although the correlation is reasonable for alkoxyamidyls (**59**), and MNDO predicts planarity for hydroxyformamidyl, oxygen substitution at a radical centre can result in deviations from planarity[41] which could be different in alkoxyaminyls and alkoxyamidyls.

Ingold and his co-workers[3,6] have ascribed the discrepancy outlined in (ii) to a small degree of twisting in simple amidyls which is not prevalent in the cyclic amidyl. However, the similarity in A_N values for aminyls and amidyls suggests that the radical-containing orbital should be orthogonal to the carbonyl group for an N-$2p_z$ coefficient of unity. This is clearly not the case.[3] While there may be some twisting in simple acyclic amidyls, we contend that it would be insufficient to account for the large A_N difference of 0.36 mT. The observed amidyl coupling must be larger as a result of mixing in the upper Σ-state. Such mixing of orthogonal energy states may be facilitated by the slight twisting shown by Ingold and co-workers to prevail in simple amidyls,[3,6] but is not possible in the more rigid cyclic amidyl (**61**) in which Π–Σ interconversion would be a symmetry-forbidden transition.

The generally observed A_N values of N-t-butylamidyls (**56**; R′ = Bu^t) are between 1.56 and 1.58 mT,[1,3,6] with that for N-t-butylformamidyl (**56**; R′ = Bu^t, R = H) as high as 1.61 mT.[5] Unless the spin-polarisation in twisted amidyls differs from that in planar amidyls there is no way of accounting for these A_N values, which are even larger than those for aminyls, unless more of the Σ-state is mixed into the Π-ground state. This would be facilitated by their greater degree of twisting.

Finally the large difference in A_N values of amidyls (**56**) and alkoxyamidyls (**59**) [point (iii)] is in accord with there being no mixing between Π- and Σ-states in alkoxyamidyls even though they are acyclic. In these radicals, as described elsewhere in this paper, and in sulphonamidyls (**57**) the energy separation between states must be the prohibiting factor. If an A_N value of 1.12 mT is representative of pure Π-state amidyls, then the difference between pure Π-alkoxyamidyls (**59**) and amidyls (**56**) would be in line with other such differences noted in point (iii). The A_N difference between the cyclic amidyl (**61**) and the cyclic oxyamidyl (**63**) is also in accord with pure Π-states for both radicals.

* Coefficients calculated by the UHF-MNDO method predict an A_N value of 1.05 mT for formamidyl.

Experimental

M.p.s were determined with a Kofler hot-stage. Mass spectra were run with a Varian MAT-212 spectrometer equipped with a Varian SS-188 data system, or on an A.E.I. MS 30 double-beam spectrometer. I.r. spectra were run with a Perkin-Elmer 297 spectrophotometer. 60 MHz N.m.r. spectra were recorded with a Perkin-Elmer R12 A spectrometer, with Me_4Si as internal standard. Preparative chromagraphic separations were carried out with a Waters Preparative LC System (h.p.l.c.) (on silica gel). Analytical separations were performed with a Waters Analytical HPLC instrument (μ-Porasil column), with a model 440 absorbance detector linked to a Waters data module.

MNDO calculations were carried out with a Burroughs 6800 computer, by use of the QCPE version of MNDO (by W. Thiel).[42]

The synthesis of N-bromo-N-methyl- and N-bromo-N-acetyl-biphenyl-2-carboxamides has been described elsewhere.[31]

N-*Methylbiphenyl-2-sulphonamide* (**37**).—Biphenyl-2-ylmagnesium iodide [from 2-iodobiphenyl (7.5 g) and Mg (0.64 g)] in ether was added dropwise to a solution of sulphuryl chloride (36 g) in hexane (100 ml) at 5 °C.[43] After 2 h at room temperature the mixture was worked up (cold water), dried, and concentrated *in vacuo*. The resultant oil was treated directly with aqueous methylamine for 4 h. Extraction with $CHCl_3$ gave, after concentration, a mixture of 2-iodobiphenyl and a dark solid which was isolated by precipitation from benzene–light petroleum. The solid in benzene (50 ml) was boiled with activated charcoal. Concentration after filtration afforded a white solid, which crystallised from benzene–light petroleum (b.p. 40—60 °C) as N-methylbiphenyl-2-sulphonamide (1.7 g), m.p. 123—125 °C (lit.,[44] 122—123 °C).

N-*Bromo*-N-*methylbiphenyl-2-sulphonamide* (**39**).—N-Methylbiphenyl-2-sulphonamide (0.58 g) was added to a solution of t-butyl hypobromite in benzene prepared by dropwise addition of bromine (1.12 g) to potassium t-butoxide (0.79 g) in benzene (30 ml). After 1.5 h in the dark, the mixture was filtered and concentrated *in vacuo* below 40 °C to an oil which crystallised to give the *bromide* (0.8 g); $\nu_{max.}(CHCl_3)$ 1 161 and 1 323 cm^{-1}; δ($CDCl_3$) 2.87 (3 H, s, NMe), 7.2—7.7 (8 H, m), and 8.1—8.37 (1 H, m) (Found: Br, 24.0. $C_{13}H_{12}BrNO_2S$ requires Br, 24.5%).

General Procedure for the Irradiation of N-*Methoxy-*, N-*Methyl- or* N-*Acetyl*-N-*halogenobiphenyl-2-carboxamides*.—A solution of the N-halogenoamide, in dry benzene (reagent grade) contained in a round-bottom Pyrex flask and cooled to room temperature in a Pyrex-walled cooling bath, was irradi-

ated with a medium-pressure mercury lamp (through Pyrex; *i.e.* >300 nm) unless otherwise specified. All irradiations were continued until tests by addition of a few drops of the mixture to aqueous potassium iodide–acetic acid solution showed no positive halogen to be present, after which the mixtures were concentrated *in vacuo* below 40 °C.

Irradiation of N-*Bromo*-N-*methylbiphenyl*-2-*carboxamide* (**7**).—(i) *Preparative, in the presence of* 3,3-*dimethylbut*-1-*ene*. *N*-Bromo-*N*-methylbiphenyl-2-carboxamide (3.42 g, 0.0118 mol) and 3,3-dimethylbut-1-ene (4.97 g, 0.59 mol) in dry benzene (100 ml) were irradiated according to the general procedure for 2.5 h. Work-up afforded a gum (2.6 g), which from its n.m.r. spectrum consisted of *N*-methylphenanthridone (**22**) (20%) (δ 3.68, s), *N*-methylbiphenyl-2-carboxamide (32%) (δ 2.65, d), and γ-lactam components (48%) (δ 2.85 and 2.95, both s). Preparative h.p.l.c. with hexane–chloroform (60:40) as eluant gave *N*-methylphenanthridone (**22**), which crystallised from benzene–light petroleum as colourless needles (0.7 g), m.p. 105—107 °C) (lit.,[19] 105—107 °C), and 4′-bromo-2-methyl-3-oxoisoindoline-1-spiro-1′-cyclohexa-2′,5′-dienes (**17**) and (**18**), from which only (**17**) crystallised (from benzene–light petroleum) as colourless prisms (0.3 g), m.p. 137—139 °C (decomp.); $\nu_{max.}$($CHCl_3$) 1 670 cm^{-1}; δ($CDCl_3$) 2.91 (3 H, s, Me), 5.25—5.45 (1 H, crude t, *J* 5 Hz, 4′-H), 5.63 (2 H, crude d, *J* 10 Hz, 2′- and 6′-H), 6.49 (2 H, dd, *J* 10 and 5 Hz, 3′- and 5′-H), and 7.40—7.98 (4 H, m, ArH); *m/z* 289/291 (M^+), 210, 195, 181, and 152.

(ii) *Analytical.* (a) *In the absence of* 3,3-*dimethylbut*-1-*ene*. *N*-Bromo-*N*-methylbiphenyl-2-carboxamide (0.37 g, 0.0013 mol) in dry benzene (50 ml) was irradiated for 30 min and gave upon work-up a gum which was shown by analytical h.p.l.c. to consist of *N*-methylbiphenyl-2-carboxamide (15%), 4′-bromo-2-methyl-3-oxoisoindoline-1-spiro-1′-cyclohexa-2′,5′-dienes (**17**) and (**18**) (65%) and *N*-methylphenanthridone (**22**) (20%); ratio Ar_2-6:Ar_1-5 0.31:1. A repeat of this reaction afforded an Ar_2-6:Ar_1-5 ratio of 0.30:1.

(b) *In the presence of* 3,3-*dimethylbut*-1-*ene*. *N*-Bromo-*N*-methylbiphenyl-2-carboxamide (0.38 g, 0.0013 mol) and 3,3-dimethylbut-1-ene (0.5 g, 0.0059 mol) in dry benzene (50 ml) were irradiated for 2.75 h and upon work-up gave a gum which was shown by analytical h.p.l.c. to consist of *N*-methylbiphenyl-2-carboxamide (32%), 4′-bromo-2-methyl-3-oxoisoindoline-1-spiro-1′-cyclohexa-2′,5′-dienes (**17**) and (**18**) (53%) and *N*-methylphenanthridone (**22**) (15%); ratio Ar_2-6:Ar_1-5 0.27:1. A repeat of this reaction afforded an Ar_2-6:Ar_1-5 ratio of 0.23:1.

Irradiation of N-*Acetyl*-N-*bromobiphenyl*-2-*carboxamide* (**8**).—(i) *In the presence of* 3,3-*dimethylbut*-1-*ene with u.v. light*. A solution of *N*-acetyl-*N*-bromobiphenyl-2-carboxamide (**8**) (2.66 g, 0.0084 mol) (84.8%) and *N*-acetylbiphenyl-2-carboxamide (0.35 g, 0.0015 mol) (15.2%) in dry benzene (50 ml) was irradiated for 2 h in the presence of 3,3-dimethylbut-1-ene (7.1 g, 0.084 mol) according to the general procedure. Work-up gave a gum which from its n.m.r. spectrum consisted of *N*-acetylphenanthridone (**23**) (24.4%), parent imide (50%), and a spirocyclised product (24.5%) (δ 2.5, s, Me and 5.2—6.4, m) which was isolated nearly pure in low yield by preparative h.p.l.c. as a colourless solid. Recrystallisation from diethyl ether afforded fine colourless needles of 2-*acetyl*-4′-*bromo*-3-*oxoisoindoline*-1-*spiro*-1′-*cyclohexa*-2′,5′-*diene* (**21**) (m.p. unknown; compound undergoes thermal decomposition at room temperature); $\nu_{max.}$($CHCl_3$) 1 700 and 1 725 cm^{-1}; δ($CDCl_3$) 2.61 (3 H, s, Me), 5.25—5.49 (1 H, crude tt, 4′-H), 5.51—5.75 (2 H, crude dd, 2′- and 6′-H), 6.15—6.51 (2 H, dd 3′-and 5′-H), and 7.29—7.80 (4 H, m, ArH); no M^+ but *m/z* 238 and 196. In a separate experiment *N*-acetylphenanthridone (**23**) was isolated by preparative h.p.l.c. as a solid. Recrystallisation from benzene–diethyl ether afforded colourless needles, m.p. 121.5—122.5 °C; $\nu_{max.}$($CHCl_3$) 1 658 and 1 740 cm^{-1}; δ($CDCl_3$) 2.74 (3 H, s, Me), 7.05—7.90 (5 H, m, ArH), 8.09—8.30 (2 H, crude d, *J* 7 Hz, ArH), and 8.30—8.52 (1 H, crude d, *J* 6 Hz, ArH) (Found: C, 75.75; H, 4.7; N, 6.15. $C_{15}H_{11}NO_2$ requires C, 75.9; H, 4.7; N, 5.9%).

(ii) *In the presence of additional bromine* (*no olefin present*) *with u.v. or visible light*. *N*-Acetyl-*N*-bromobiphenyl-2-carboxamide (**8**) (1.34 g, 0.0042 mol) and bromine (1.34 g, 0.0084 mol) in dry benzene (50 ml) were irradiated for 2 h and after work-up afforded a gum. Analysis of its n.m.r. spectrum indicated the presence of parent imide (47%) (δ 2.27, 3 H, s, Me) and cyclic products (53%) (methyl singlets at δ 2.67, 2.71, and 2.77 as well as a complex olefinic region 4.2—6.4). Analytical h.p.l.c. showed the presence of *N*-acetylphenanthridone (**23**) and at least five other products. Separation by preparative h.p.l.c. and t.l.c. afforded five crystalline components, each of which was recrystallised from benzene–light petroleum and listed in order of increasing polarity.

(a) 2-*Acetyl*-2′,2′,3′,4′-*tetrabromo*-3-*oxoisoindoline*-1-*spiro*-1′-*cyclohex*-5′-*ene* (**30**) (10 mg), m.p. 155—156 °C; $\nu_{max.}$($CHCl_3$) 1 695 and 1 745 cm^{-1}; δ($CDCl_3$) 2.83 (3 H, s, Me), 5.08 (1 H, ddd, *J* 9.3 and 1.7 Hz, 5′-H), 5.98 (1 H, d, *J* 9 Hz, 6′-H), 6.29 (1 H, dd, *J* 3 and 2.3 Hz, 4′-H), 6.65 (1 H, dd, *J* 1.7 and 2.3 Hz, 3′-H), and 7.3—8.2 (4 H, m, ArH); *m/z* (^{79}Br) 474, 432, 415, 352, 336, 274, 273, and 195 (Found: C, 32.4; H, 2.05; N, 2.6. $C_{15}H_{11}Br_4NO_2$ requires C, 32.35; H, 2.0; N, 2.5%).

(b) 2-*Acetyl*-3′,3′,4′-*tribromo*-3-*oxoisoindoline*-1-*spiro*-1′-*cyclohex*-5′-*ene* (**31**) (40 mg), m.p. 201—206 °C (decomp.); $\nu_{max.}$($CHCl_3$) 1 690 and 1 742 cm^{-1}; δ($CDCl_3$) 2.75 (3 H, s, Me), 5.07 (1 H, dd, *J* 9.5 and 3.5 Hz, 5′-H), 5.84 (1 H, d, *J* 9.5 Hz, 6′-H), 6.2 (2 H, s, 2′-H_2), 6.4 (1 H, br d, 4′-H), and 7.5—8.2 (4 H, m, ArH); *m/z* (^{79}Br) 396, 354, 337, 274, 258, 196, and 195 (Found: C, 37.35; H, 2.45; N, 2.9. $C_{15}H_{12}Br_3NO_2$ requires C, 37.7; H, 2.5; N, 2.9%).

(c) 2-*Acetyl*-2′,3′,4′,5′,6′-*pentabromo*-3-*oxoisoindoline*-1-*spiro*-1′-*cyclohexane* (**33**) (80 mg), m.p. 161—172 °C (decomp.); $\nu_{max.}$($CHCl_3$) 1 708 and 1 714 cm^{-1}; δ($CDCl_3$) 2.83 (3 H, s, Me), 4.9—5.2 (3 H, m, 3′-, 4′-, and 5′-H), 5.48 (1 H, d, *J* 6.3 Hz, 2′- or 6′-H), 6.15 (1 H, d, *J* 1.8 Hz, 6′- or 2′-H), 7.35—7.85 (2 H, m, ArH), 8.15—8.30 (1 H, m, ArH), and 8.63—8.85 (1 H, m, ArH); *m/z* (^{79}Br) 512, 432, 354, 274, 273, and 195 (Found: C, 28.45; H, 1.95; N, 2.2. $C_{15}H_{12}Br_5NO_2$ requires C, 28.25; H, 1.9; N, 2.2%).

(d) A tribromo-2-acetyl-3-oxoisoindoline-1-spiro-1′-cyclohexene (100 mg), m.p. 194—196 °C (decomp.); $\nu_{max.}$($CHCl_3$) 1 693 and 1 742 cm^{-1}; δ($CDCl_3$) 2.76 (3 H, s, Me), 4.7—6.6 (5 H, m), and 7.4—8.2 (4 H, m, ArH); *m/z* (^{79}Br) 396, 354, 337, 275, 274, 196, and 195 (Found: C, 37.25; H, 2.55; N, 2.8. Calc for $C_{15}H_{12}Br_3NO_2$: C, 37.7; H, 2.5; N, 2.9%).

(e) 2-*Acetyl*-2′,3′,4′-*tribromo*-3-*oxoisoindoline*-1-*spiro*-1′-*cyclohex*-5′-*ene* (**32**) (240 mg), m.p. 156 °C (decomp.); $\nu_{max.}$($CHCl_3$) 1 695 and 1 740 cm^{-1}; δ($CDCl_3$) 2.69 (3 H, s, Me), 5.14 (1 H, ddd, *J* 4.4, 1.2, and 1.6 Hz, 3′-H), 5.37 (1 H, dd, *J* 5 and 1.6 Hz, 4′-H), 5.79 (d, *J* 10 Hz, 6′-H), 6.16 (1 H, d, *J* 4.4 Hz, 2′-H), 6.2 (1 H, ddd, *J* 10.5 and 1.2 Hz, 5′-H), 7.5—7.9 (2 H, m, ArH), 7.88—8.03 (1 H, m, ArH), and 8.16—8.32 (1 H, m, ArH); *m/z* 475 (M^+), 396, 354, 337, 274, 258, 196, and 195 (Found: C, 37.65; H, 2.55; N, 2.85. $C_{15}H_{12}Br_3NO_2$ requires C, 37.7; H, 2.5; N, 2.9%).

Irradiation of N-*Chloro*-N-*methoxybiphenyl*-2-*carboxamide* (**10**) *in an Adamantane Matrix*.— The matrix was prepared from a benzene (50 ml) solution of adamantane (2.0 g, 0.0146 mol) and *N*-chloro-*N*-methoxybiphenyl-2-carboxamide (**10**) (0.092 g, 3.51×10^{-4} mol) by removal of the solvent *in vacuo* in the dark below 40 °C. U.v. irradiation at room temperature and analysis by means of h.p.l.c. gave the following results.

(i) Before reaction: *N*-methoxyphenanthridone (**24**) (1.7%).

(ii) After irradiation for 5 h: *N*-methoxyphenanthridone (**24**) (1.7%); *N*-methoxybiphenyl-2-carboxamide (**34**) (27.8%); methyl biphenyl-2-carboxylate (**36**) (48.3%); *N,N'*-dimethoxy-*N,N'*-bis(biphenyl-2-ylcarbonyl)hydrazine (**35**)[31] (0%).

An identical matrix left in the dark at room temperature gave the following results after 5 h: *N*-methoxyphenanthridone (**24**) (2.7%); *N*-methoxybiphenyl-2-carboxamide (**34**) (14.1%); *N*-chloro-*N*-methoxybiphenyl-2-carboxamide (**10**) (83.1%) (by iodometry).

Quantitative Comparison: Photolysis of N-*Bromo*-N-*methylbiphenyl-2-carboxamide* (**7**).—A solution of *N*-bromo-*N*-methylbiphenyl-2-carboxamide (**7**) (1.00 g, 0.0034 mol) and 3,3-dimethylbut-1-ene (1.45 g, 0.0172 mol) in benzene (40 ml) was irradiated with a medium-pressure mercury lamp through Pyrex for 3 h. Independently, *N*-bromo-*N*-methylbiphenyl-2-carboxamide (**7**) (1.00 g, 0.0034 mol) in an adamantane (5.00 g) matrix was irradiated with a medium-pressure mercury lamp through Pyrex for 3 h. Analysis of the two reaction mixtures by h.p.l.c. showed them both to contain *N*-methylbiphenyl-2-carboxamide, 4'-bromo-2-methyl-3-oxoisoindoline-1-spiro-1'-cyclohexa-2',5'-dienes (**17**) and (**18**), and *N*-methylphenanthridone (**22**), in similar yields (±5%) of 32, 53, and 15%, respectively.

Cyclisations of N-*Methylbiphenyl-2-sulphonamide* (**37**).—(a) *Irradiation of* N-*iodo*-N-*methylbiphenyl-2-sulphonamide* (**38**) in situ. t-Butyl hypochlorite (2.51 g) and potassium t-butoxide (2.65 g) were added with stirring at 10 min intervals to finely ground iodine (5.96 g) in t-butyl alcohol (25 ml). During addition the two-necked flask was cooled in a water-bath at room temperature and all light was excluded. *N*-Methylbiphenyl-2-sulphonamide (0.58 g, 2.35×10^{-3} mol) was added, and after being stirred in the dark for a further 10 min the mixture was irradiated (1 000 W tungsten lamp) at room temperature for 4 h. The mixture was poured into an excess of aqueous sodium thiosulphate, which was extracted with chloroform (2 × 50 ml). The combined extracts were washed (water), dried (Na_2SO_4), and concentrated to an oil (1 g), which contained residual t-butyl alcohol and parent sulphonamide [δ($CDCl_3$) 2.32 (3 H, d, NH*Me*)], and also displayed a singlet in the n.m.r. spectrum at δ 3.41. The mixture was separated by preparative h.p.l.c. into two components: *N*-methylbiphenyl-2-sulphonamide (**37**) (0.33 g), identical (i.r., n.m.r., and m.p.) with authentic material, and 2-methyldibenzo[*c,e*][1,2]thiazine 1,1-dioxide (0.124 g), which crystallised from benzene–light petroleum (b.p. 40—60 °C) as prisms, m.p. 112—114 °C (lit.,[44] 110.5—111.5 °C); $\nu_{max.}$($CDCl_3$) 1 165 and 1 322 cm^{-1}; δ($CDCl_3$) 3.41 (3 H, s, NMe) and 7.1—8.14 (8 H, m, ArH).

(b) *Dark reaction of* N-*iodo*-N-*methylbiphenyl-2-sulphonamide*. A reaction mixture identical with that in (a) was stirred in the dark for 4 h. Identical work-up afforded only unchanged *N*-methylbiphenyl-2-sulphonamide (n.m.r., t.l.c.).

(c) *Irradiation of* N-*bromo*-N-*methylbiphenyl-2-sulphonamide* (**39**). A solution of *N*-bromo-*N*-methylbiphenyl-2-sulphonamide (0.6 g, 1.84×10^{-3} mol) in dry benzene (50 ml) was divided into two portions. 3,3-Dimethylbut-1-ene (0.77 g, 9.2×10^{-3} mol) was added to one portion and both were then degassed by the freeze–thaw method and irradiated with a medium-pressure Hg lamp at room temperature under nitrogen for 45 min. The mixtures were concentrated *in vacuo* and analysed by n.m.r., which indicated the presence of only 2-methyldibenzo[*c,e*][1,2]thiazine 1,1-dioxide (**41**) (δ 3.4, s) and *N*-methylbiphenyl-2-sulphonamide (**37**) (δ 2.3, d). Analysis by h.p.l.c. indicated the formation of sultam and sulphonamide in yields of 50 and 46% (no 3,3-dimethylbut-1-ene) and 50 and 39% (olefin present), respectively.

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