Reactions of Condensed *N*-Heteroaromatic Molecules. Part III.[1] Photochemical Reactivity and Acylation of *N*-Acyldibenz[*b,f*]azepines and Derivatives

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Unsensitised and benzophenone-sensitised irradiation of *N*-acyl, -aroyl, -carbamoyl, and -ethoxycarbonyl derivatives of 5*H*-dibenz[*b,f*]azepine (1) (iminostilbene) gives good yields of tetrabenzo[*b,b',f,f'*]cyclobuta[1,2-*d*:3,4-*d'*]-bisazepines (14)—(19). Similarly, mixed cycloadducts are formed with *N*-methyl- and *N*-phenyl-maleimide. Quenching experiments suggest that triplet states of the iminostilbene derivatives are involved, and it is thought that the mixed cycloadducts arise *via* exciplexes. In contrast, the parent compound (1) and its *N*-alkyl derivatives are photochemically inactive, whereas the *N*-tosyl compound undergoes photo-Fries rearrangement. Although electrophilic substitution in dibenz[*b,f*]azepine apparently occurs at the 2- and 8-positions, the 5-acetyl derivative undergoes Friedel–Crafts acylation exclusively at the 10(11)-position. Photoelectron spectra reveal that ionisation potentials of *N*-alkyldibenzazepines are considerably less than those of the corresponding *N*-acyl derivatives.

INTEREST in the 5*H*-dibenz[*b,f*]azepine ring system centres around derivatives having γ-dialkylaminopropyl substituents at the 5-position, which are pharmacologically active as anti-depressants.[2] Much of the reported chemistry of this ring system is to be found in the patent literature, and is limited mainly to descriptions of the syntheses of 5-substituted derivatives; spectral properties and fundamental chemistry have as yet not been fully reported.[3]

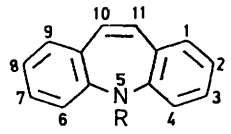
We now present the results of examination of the photochemical behaviour and Friedel–Crafts acylation of a number of derivatives of 5*H*-dibenz[*b,f*]azepine (iminostilbene) (1).

Photochemistry of N-*Acyldibenz*[b,f]*azepines.*—Literature descriptions of the photochemistry of 5*H*-dibenz-[*b,f*]azepines are restricted to the parent compound (1) and the 5-nitroso-derivatives (2). Both materials were found to be photostable in an inert atmosphere but irradiation of the latter in the presence of oxygen afforded 2-nitrodibenz[*b,f*]azepine (25).[4]

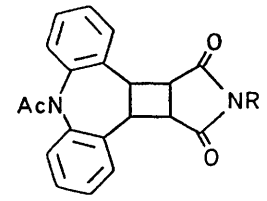
Irradiation of degassed solutions of 5-acetyldibenzazepine (3) in acetone or benzene (*in vacuo*) produced a crystalline precipitate of the dimer (14).[5] The i.r. spectrum of this material lacked olefinic absorptions at 810 cm^{-1} (etheno-bridge) and the mass spectrum exhibited a molecular ion at *m/e* 470. The benzophenone-sensitised

[1] Part II, L. J. Kricka and A. Ledwith, *J.C.S. Perkin I*, 1973, 859.
[2] E. Jucker, *Angew. Chem. Internat. Edn.*, 1963, **2**, 493.
[3] L. J. Kricka and A. Ledwith, *Chem. Rev.*, 1974, in the press.
[4] M. R. Bendall, J. B. Bremner, and J. F. W. Fay, *Austral. J. Chem.*, 1972, **25**, 2451.
[5] L. J. Kricka, M. C. Lambert, and A. Ledwith, *J.C.S. Chem. Comm.*, 1973, 244.

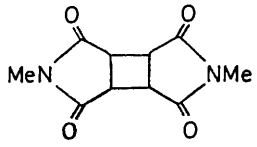
reaction gives a quantitative yield of dimer in 0·5 h, but the unsensitised reaction is less efficient (36% after 1 h). In both cases, penta-1,3-diene or dissolved air (O_2) retards the photodimerisation, suggesting the involvement of triplet intermediates. Michler's ketone (E_T 61·0 kcal mol^{-1}), but not fluorenone (53·3 kcal mol^{-1}), was found to sensitise the dimerisation in acetone or benzene,



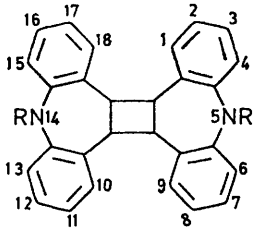
(1) R=H
(2) R=NO
(3) R=Ac
(4) R=COEt
(5) R=CO·CH_2Cl
(6) R=COPh
(7) R=CO_2Et
(8) R=CO·NH_2
(9) R=Me
(10) R=Et
(11) R=Pr^n
(12) R=SO_2·C_6H_4Me-*p*
(13) R=$[CH_2]_3$·NMe_2



(20) R=Me
(21) R=Ph



(22)



(14) R=Ac
(15) R=COEt
(16) R=CO·CH_2Cl
(17) R=COPh
(18) R=CO_2Et
(19) R=CO·NH_2

indicating that E_T for (3) lies in the region 53·3—61·0 kcal mol^{-1}.

Similarly, sensitised irradiation of 5-propionyl- (4), 5-chloroacetyl- (5), 5-benzoyl- (6), 5-ethoxycarbonyl- (7), and 5-carbamoyl-dibenz[*b*,*f*]azepine (8) gave the dimers (15)—(19). Only one type of dimer was isolated from each substrate; this, taken with the presumed intermediacy of triplet state reactants, leads to an assumption of a thermodynamically stable *trans*-configuration for the cyclo-dimers.[6]

Sensitised and unsensitised irradiations of the parent (1) and *N*-alkyl dibenzazepines [*e.g.* (10)] resulted in no change. The lowest energy transition in these compounds ($\lambda_{max.}$ 365 nm), which gives rise to their yellow colour, is (presumably) $n \longrightarrow \pi^*$ in character.[7] The derivatives which photodimerised [(3)—(8)] carry substituents which lower the energy of the non-bonding electron pair on the nitrogen atom, as evidenced by their u.v. spectra and absence of colour, and show photoreactivity similar to that of *cis*-stilbene analogues (see later).

Irradiation of a benzophenone-sensitised solution of 5-acetyldibenz[*b*,*f*]azepine (3) * in acetone containing *N*-methylmaleimide afforded the mixed dimer (20), together with the homo-dimer (14). The mass spectrum of the crude product indicated that a further contaminant was the homo-dimer of *N*-methylmaleimide (22). As with the homo-dimerisation of 5-acyldibenzazepines, only one type of mixed adduct was isolated, and this is presumed to have *trans*-stereochemistry. The n.m.r. spectrum of (20) at room temperature exhibited a complex absorption in the region appropriate to cyclobutane ring protons; the complexity of the spectrum is attributed to inversion of the azepine ring.[9]

A mixed dimer (21) was also isolated from the photoreaction of (3) with *N*-phenylmaleimide. Mass spectral analysis indicated that mixed dimers were also formed with dimethyl maleate and dichloromaleic anhydride, respectively; but these mixed dimers could not be separated from the complex mixtures of photoproducts.

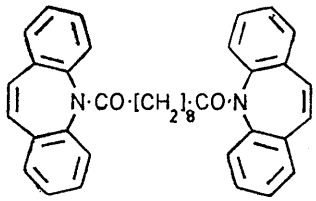
No adducts were obtained from the benzophenone-sensitised reactions of (3) with substrates having a wide range of triplet state energy values, *e.g.* acrylonitrile (acceptor molecule), isobutyl vinyl ether (donor molecule), styrene, dimethyl fumarate, and acetylenedicarboxylic acid. It is possible therefore that the mixed cycloadditions proceed *via* formation of exciplexes, favoured by a combination of electronic and steric factors, between either ground state (3) and triplet addend, or triplet (3) and ground state addend. This is in contrast to photocycloadditions of olefins to the 2,3-double bond of *N*-acylindoles, which are thought to proceed *via* a triplet indole species.[10]

Benzophenone-sensitised irradiation of a solution of 5,5'-decanedioylbisdibenz[*b*,*f*]azepine (23) in acetone afforded insoluble crystalline material which was tentatively identified as the dimer (24) on the basis of i.r. and mass spectral evidence. The related *NN'*-polymethylenebismaleimides have been shown [11] to undergo analogous photodimerisations and photopolymerisations.

* Careful purification of (3) was necessary, as a pale yellow impurity, with strong violet fluorescence in methanol, was found to sensitise the dimerisation. The mass spectrum of an impure sample of (3) indicated that the fluorescent impurity was probably 9(10*H*)-acridone (*m/e* 195), which arises *via* oxidative ring contraction of (3) under the acidic acetylation conditions.[8] The related compound 10-methyl-9(10*H*)-acridone was found to sensitise the dimerisation.

[6] D. Seebach in ' Methoden Der Organischen Chemie (Houben-Weyl),' Thieme Verlag, Stuttgart, 1971, vol. 4/4.
[7] R. W. Schmid, *Helv. Chim. Acta*, 1962, **45**, 1982.
[8] L. J. Kricka and A. Ledwith, unpublished results.
[9] R. J. Abraham, L. J. Kricka, and A. Ledwith, *J.C.S. Chem. Comm.*, 1973, 282.
[10] D. R. Julian and R. Foster, *J.C.S. Chem. Comm.*, 1973, 311.
[11] F. C. de Schryver, W. J. Feast, and G. Smets, *J. Polymer Sci., Part A—I, Polymer Chem.*, 1970, **8**, 1939.

In contrast with the behaviour of 5-acyliminodibenz[*b*,*f*]azepines,* unsensitised irradiation of 5-tosyliminostilbene (12) afforded 2-tosyliminostilbene (26) in low



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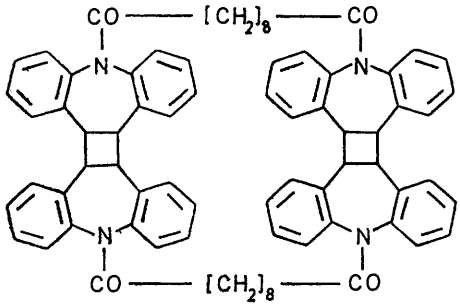

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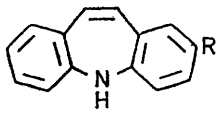
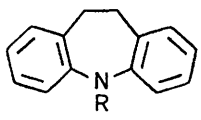
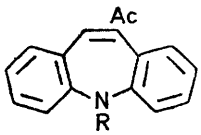


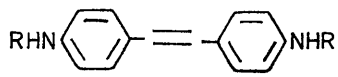
(25) R=NO_2
(26) R=$SO_2C_6H_4Me$-*p*



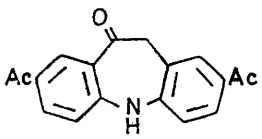
(31) R=H
(32) R=Ac
(33) R=Me



(27) R=Ac
(28) R=CO·CH_2Cl
(29) R=COEt



(34) R=H
(35) R=Ac



(30)

conversion. This material was isolated by column chromatography; the location of the tosyl group is assumed by analogy with the related photo-Fries rearrangement of sulpho-anilides, shown to yield exclusively *para*-tosylanilines.[12] In the mass spectra, fragmentation of the molecular ion *via* loss of a tosyl group is only of minor importance for (26), whereas for the 5-tosyl isomer (12) this is the principal mode of fragmentation, providing the base peak. These observations reflect the relative strengths of the *C*- and *N*-tosyl links.

Acylation of N-*Acyldibenz*[b,f]*azepines.*—The reaction of 5-acetyldibenz[*b*,*f*]azepine (3) with acetyl chloride–aluminium trichloride in carbon disulphide afforded 5,10-diacetyldibenz[*b*,*f*]azepine (27), the i.r. spectrum of which lacked absorption at 810 cm^{-1} (CH=CH) and showed a new absorption at 900 cm^{-1}, appropriate to a trisubstituted olefinic bond.[13] Similarly 5-chloroacetyl- (5) and 5-propionyl-dibenz[*b*,*f*]azepine (4) afforded 10-acetyl-5-chloroacetyl- and 5-propionyl-dibenz[*b*,*f*]azepine [(28 and (29)]. In the n.m.r. spectra of the 10-acetyl derivatives (27)—(29), the 11-proton absorbs in the region τ 2·2—2·3; the downfield shift (see Table 2) is comparable to that for β-acetylstyrene[14] (α-H τ 2·55; *cf.* styrene,[15] α-H τ 3·31).

The observed deactivation of the aromatic rings by *N*-acylation is supported by π-electron densities (ρ) calculated for the 5-acetyldibenzazepine molecule, which predict that electrophilic attack should occur preferentially at the 10-position (*cf.* Friedel–Crafts acylation of stilbene, which occurs in the aromatic rings at the 4- and 4′-positions[16]).

In the only reported example of an electrophilic substitution of dibenz[*b*,*f*]azepine,[17] reaction with 2,4,4-trimethylpent-1-ene–aluminium trichloride at 180—190° afforded 2-t-butyl and 2,8-di-t-butyl derivatives. However, we have found that 5-methyldibenzazepine is unreactive towards electrophilic acylation, either by acetylium perchlorate generated *in situ*, or by acetyl chloride–aluminium trichloride with nitrobenzene (homogeneous conditions) or carbon disulphide (heterogeneous conditions) as solvent. A trace product from the latter reaction was tentatively identified as 2,8-diacetyldibenz[*b*,*f*]azepin-10(11*H*)-one (30) on the basis of spectral evidence and an accurate mass measurement of the molecular ion (see Experimental section).

Attempted hydrolysis of the amides (27) and (28) under acidic and basic conditions, respectively, gave only intractable tars, and it is notable that 5-acetyldibenzazepine is inert to both acidic and basic hydrolysis,† under conditions in which the structurally related 5-acetyl-10,11-dihydrodibenzazepine and *N*-acetylcarbazole are readily deacetylated. Also, whereas *N*-acetylcarbazole may be reduced by aluminium isoproproxide

* J. B. Bremner (University of Tasmania) has informed us that photo-Fries rearrangement of (3), to give low yields of 2- and 4-acetyldibenzazepine, occurs on irradiation in degassed ethanol. In our hands photo-Fries products (which are readily detected by their colour) were not observed at all for sensitised and unsensitised irradiations in benzene or acetone. Unsensitised photodimerisation in ethanol was accompanied by slight yellowing of the solutions, whereas benzophenone-sensitised reactions, in the same solvents, showed no evidence for photo-Fries rearrangements. We are grateful to Dr. Bremner for this personal communication.

† The *N*-acetyl group may be removed by prolonged refluxing with ethanolic potassium hydroxide.

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[13] L. J. Bellamy, ' The Infra-red Spectra of Complex Molecules,' Methuen, London, 1958; p. 34 *et seq.*
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[15] F. A. Bovey, ' N.m.r. Data Tables for Organic Compounds,' Interscience, London, 1967.
[16] W. C. J. Ross, *J. Chem. Soc.*, 1945, 536.
[17] Geigy AG, Belg.P. 659,527/1965 (*Chem. Abs.*, 1966, **64**, 739c).

in refluxing xylene to give carbazole and acetaldehyde (not detected), 5-acetyldibenzazepine is unchanged in these conditions. This anomalous behaviour may be explained by assuming that the latter molecule is best described electronically by a canonical structure in which the amide bond is completely polarised *e.g.* $>\overset{+}{N}=\underset{|}{C}-O^-$ (*cf.* acid-catalysed hydrolysis of ethyl 1*H*-azepine-1-carboxylate [18]). The adoption of dibenzazepinium character by 5-acetylated dibenzazepine derivatives is energetically favourable, since the anti-aromatic 8 π-electron azepine ring system is thereby transformed, by delocalisation of the nitrogen lone pair electrons towards the more electronegative oxygen atom, into an aromatic 6 π-electron system (*cf.* the tropylium cation [19]).

Evidence for the dibenzazepinium character of 5-acyldibenzazepines is available from comparison of the electronic absorption spectra of 5-methyl- [$\lambda_{max.}$ (MeOH) 213 (ϵ 17,900), 259 (36,100), 290sh (5950), and 340sh nm (1500)], and 5-acetyl-dibenzazepines [238sh (16,850), 286 (12,500), 380 (57), and 398 nm (58)], which are markedly different; the spectrum of the latter is similar to that of *cis*-stilbene [225 (20,400) and 278 nm (9400)], indicating that the nitrogen lone pair electrons of 5-acetylated derivatives do not interact appreciably with the stilbene chromophore present in the dibenz[*b,f*]azepine nucleus.

Photoelectron spectra reveal similar electronic differences between 5-alkyl and 5-acyl derivatives of dibenz[*b,f*]azepine and its 10,11-dihydro-derivative (Table 1).

TABLE 1

Vertical and adiabatic ionisation potentials (in eV) of dibenz[*b,f*]azepine derivatives

Compound	Vertical I.P. values; adiabatic I.P.s in parentheses
(1)	7·10 (6·65), 8·13 (7·90), 8·99, 10·46
(3)	8·13, 8·77, 9·40, 10·78
(9)	7·02 (6·60), 7·90 (7·65), 8·98, 10·46
(13)	6·92 (6·55), 7·95, 9·63
(31)	7·00 (6·70), 8·71 (8·30), 10·45
(32)	8·65, 9·91
(33)	7·10 (6·74), 8·56 (8·00), 9·91 (9·60)
cis-Stilbene	7·90 (7·50), 8·82 (8·62), 10·07

The ionisation potential of 5-acetyldibenzazepine is greater, by more than 1 eV than that of the 5-methyl analogue. The apparently low ionisation potential recorded for 5-(γ-dimethylaminopropyl)dibenzazepine (**13**) may have some special significance in view of the pharmacological activity of this material.[20]

^{1}H N.m.r. spectra of a series of dibenz[*b,f*]azepine derivatives are collected in Table 2. The shift to lower field of the absorption appropriate to the etheno-bridge protons upon acylation of the nitrogen atom is unexceptional; *N*-acetylation of 4,4'-diaminostilbene (**34**) [τ 3·26 (CH=CH)] also causes the etheno-proton signal to shift to lower field (τ 2·97).

TABLE 2

^{1}H N.m.r. spectra (τ values; *J* in Hz) of 5*H*-dibenz[*b,f*]azepine derivatives

	CH= (s)	ArH (m)	Others
(1)	3·75 (2H)	2·8—3·3 (8H)	
(3)	3·12 (2H)	2·5—2·8 (8H)	8·16 (3H, s, NAc)
(5)	3·14 (2H)	2·5—2·8 (8H)	6·25 (2H, d, CO·CH$_2$Cl)
(4)	3·18 (2H)	2·5—2·9 (8H)	7·90 (2H, m, CO·CH$_2$), 9·00 (3H, t, *J* 7, Me)
(9)	3·32 (2H)	2·7—3·2 (8H)	6·70 (3H, s, NMe)
(10)	3·32 (2H)	2·7—3·2 (8H)	6·25 (2H, q, *J* 6, CO·CH$_2$), 8·82 (3H, t, Me)
(11)	3·45 (2H)	2·8—3·5 (8H)	6·40 (2H, t, *J* 6, N·CH$_2$), 8·45 (2H, m, CH$_2$), 9·10 (3H, t, Me)
(6)		2·6—3·0 (15H)	
(2)	3·29 (2H)	2·5—3·0 (8H)	
(27)	2·30 (1H)	2·5—2·7 (8H)	7·44, 7·55 (each 3H, s, Ac), 8·90, 8·12 (each 3H, s, NAc)
(28)	2·20 (1H)	2·5—2·6 (8H)	6·05, 6·13 (each 2H, s, N·CO·CH$_2$), 7·45 (3H, s, Ac)
(29)	2·19 (1H)	2·4—2·7 (8H)	7·41, 7·42 (each 3H, s, Ac), 7·8br (2H, N·CH$_2$), 9·00 (3H, t, *J* 7, Me)
(12)	3·84 (2H)	2·5—3·0 (12H)	7·64 (3H, s, Me)
(26)	4·15 (2H)	2·1—3·5 (11H)	7·60 (3H, s, ArMe)

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls. Mass spectra were measured by the Physico-Chemical Measurements Unit, Harwell. ^{1}H N.m.r. spectra were recorded at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Photoelectron spectra were recorded on a Perkin-Elmer spectrometer with argon and xenon as internal references. Alumina for chromatography was Brockmann Grade I, neutral (B.D.H.).

SCFMO calculations were carried out by the method of Pople, Pariser, and Parr,[21] using the appropriate atomic parameters,[22] repulsion integrals,[23] and core resonance integrals.[24]

5-Methyldibenz[*b,f*]azepine (79%), m.p. 141—143° (lit.,[25] 143—144·5°), was prepared as described previously.[1] 5-Acetyldibenz[*b,f*]azepine, m.p. 116—118° (lit.,[26] 117—119°), and 5-chloroacetyldibenz[*b,f*]azepine, m.p. 145—146° (lit.,[27] 147—148°), were prepared by acylation of 5*H*-dibenz[*b,f*]-azepine, as reported. Similarly prepared were 5-propionyl-dibenz[*b,f*]azepine (90%), m.p. 66—67° (lit.,[28] 75·7°) [from petroleum (b.p. 40—60°)–ether (9 : 1 v/v)] (Found: C, 81·8; H, 6·0; N, 5·7. Calc. for $C_{17}H_{15}NO$: C, 81·9; H, 6·1; N, 5·6%), $\nu_{max.}$ 1680br (C=O), 1600, 1498, 1115, 1280br, 1185, 805 (CH=CH), and 770 cm^{-1}, *m/e* 249 (M^+, 31%), 250 (M + 1, 7), 194 (18), 193 ($M - C_3H_4O$, 100), 192 (M − COEt, 56), 191 (16), and 165 (9), m^* 150 (249 $\longrightarrow$ 193); and 5-*benzoyldibenz*[b,f]*azepine* (26%), m.p. 131—132°, as prisms (from ether) (Found: C, 84·8; H, 5·0; N, 4·9. $C_{21}H_{15}NO$ requires C, 84·8; H, 5·1; N, 4·7%), $\nu_{max.}$ 1660 (C=O), 1620,

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[23] N. Mataga and K. Nishimoto, *Z. phys. Chem.* (*Frankfurt*), 1956, **12**, 335; 1957, **13**, 140.
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[25] R. Huisgen, E. Laschtuvka, and F. Bayerlein, *Chem. Ber.*, 1960, **93**, 392.
[26] W. Schindler and H. Blattner, *Helv. Chim. Acta*, 1961, **44**, 753.
[27] Geigy AG, B.P. 849,032/1960 (*Chem. Abs.*, 1961, **55**, 8436g).
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1600, 1499, 1270, 1125, 1115, 895, 880, 802 (CH=CH), 770, and 750 cm^{-1}, *m/e* 297 (M^+, 21%), 193 (14), 192 (M − PhCO, 71), 191 (21), 165 (14), 105 ($PhCO^+$, 100), 83 (24), and 77 (36), *m** 142 (192 ⟶ 165).

Ethyl dibenz[*b,f*]azepine-5-carboxylate (20%), m.p. 124—126° (lit.,[26] 126—128°), was prepared from the sodium salt of dibenz[*b,f*]azepine and ethyl chloroformate.

5-p-*Tolylsulphonyldibenz*[b,f]*azepine*.— Toluene-*p*-sulphonyl chloride (25 g) was added to a solution of dibenz[*b,f*]-azepine (10 g) in dry pyridine (60 ml). The mixture was refluxed for 0·5 h, cooled, and then poured into water. The precipitate was filtered off, washed with water, and recrystallised from ethanol to afford *prisms* (14 g, 78%), m.p. 166—167° (Found: C, 72·5; H, 5·0; N, 4·0; S, 9·2. $C_{21}H_{17}NO_2S$ requires C, 72·6; H, 4·9; N, 4·0; S, 9·2%), $\nu_{max.}$ 1600, 1495, 1160br, 1100, 1090, 970, 865, 800, 770, and 605 cm^{-1}, *m/e* 347 (M^+, 3%), 193 (40), 192 (M − $SO_2{\cdot}C_6H_4Me$, 100), 191 (30), and 165 (32).

5,5′-*Decanedioylbisdibenz*[b,f]*azepine* (23).—Decanedioyl dichloride (4·8 g) was added dropwise to a stirred solution of dibenz[*b,f*]azepine (8·0 g) in benzene (50 ml). The mixture was refluxed for 5 h, cooled, and then poured into water. The aqueous mixture was extracted with dichloromethane and the extract washed with water and dried ($MgSO_4$). Evaporation afforded a yellow oil which was recrystallised from benzene–ether (1 : 1 v/v), to give the crude product (8·5 g). This was redissolved in the minimum amount of chloroform and chromatographed on a column of neutral alumina (250 g) made up in petroleum and eluted with petroleum and petroleum–benzene. Benzene–methanol (9 : 1 v/v) eluted the *diamide* (5·0 g, 46%), m.p. 137—138° (from ethanol) (Found: C, 82·4; H, 6·5; N, 5·0. $C_{38}H_{36}N_2O_2$ requires C, 82·6; H, 6·6; N, 5·1%), $\nu_{max.}$ 1660br (C=O), 1595, 1490, 1300br, 1250, 1160, 878, 864, 800, 795, 765, and 755 cm^{-1}, τ 2·5—2·8 (16H, s, ArH), 3·20 (4H, s, HC=CH), 7·7—8·2br (4H, $CO{\cdot}CH_2$), and 8·4—9·1br (12H, CH_2), *m/e* 552 (M^+, <1%), 361 (25), 360 (100), 194 (25), 193 (94), and 192 (31).

4,4′-Diacetamidostilbene was prepared by treatment of a suspension of 4,4′-diaminostilbene (3·0 g) in aqueous hydrochloric acid with acetic anhydride (5 ml). The crude product was dissolved in hot dimethylformamide, and the solution was cooled and poured into water. The *precipitate* was filtered off and dried (yield 3·5 g, 85%), m.p. 331—333° (lit.,[29] 312°) (Found: C, 73·3; H, 6·2; N, 9·7. Calc. for $C_{18}H_{18}N_2O_2$: C, 73·4; H, 6·2; N, 9·5%), $\nu_{max.}$ 3320 (N–H), 1670 (C=O), 1610, 1545, 975, and 840 cm^{-1}, τ [$(CD_3)_2SO$] 2·4—2·5 (8H, s, ArH), 2·90 (2H, s, HC=CH), 6·52 (2H, s, NH), and 7·92 (6H, s, Ac), *m/e* 294 (M^+, 100%), 295 (M + 1, 18), 253 (7), 252 (41), 211 (8), 210 (37), and 209 (13), *m** *ca.* 216 (294 ⟶ 252) and *ca.* 175 (252 ⟶ 210).

Photodimerisation of 5-Acetyldibenz[b,f]*azepine* (*Typical Procedure*).—A Pyrex tube containing a degassed solution (six freeze–thaw cycles) of 5-acetyldibenz[*b,f*]azepine (200 mg) and benzophenone (200 mg) in acetone (14 ml) was sealed under vacuum and irradiated (Hanovia Reading Reactor) for 5 min. The crystalline material deposited was filtered off and dried to afford 5,14-*diacetyl*-9b,9c,18b,18c-*tetrahydrotetrabenzo*[b,b′,f,f′]*cyclobuta*[1,2-d:3,4-d′]*bisazepine* (14) (154 mg, 77%), m.p. 342—345° (Found: C, 81·7; H, 5·7; N, 5·8. $C_{30}H_{26}N_2O_2$ requires C, 81·7; H, 5·6; N, 6·0%), $\nu_{max.}$ 1670 (C=O), 1505, 1340, 785, 770, and 750 cm^{-1}, τ (H_2SO_4) (all absorptions broad) 1·9—2·8 (16H, ArH), 5·6 (4H, CH), and 6·6 (6H, Ac), *m/e* 470 (M^+, <1%), 428 (M − C_2H_2O, <1), 236 (18), 235 (66), 194 (23), 193 (100), 192 (50), 180 (15), and 165 (14), *m** 159 (235 ⟶ 193).

Similarly prepared were the 5,14-*dipropionyl analogue* (15) (80%), m.p. 323—325° (Found: C, 81·8; H, 6·0; N, 5·6. $C_{32}H_{30}N_2O_2$ requires C, 81·9; H, 6·1; N, 5·6%), $\nu_{max.}$ 1670 (C=O), 1498, 1300, 1280, 1180, 780, 765, 760, and 740 cm^{-1}, *m/e* 498 (M^+, <1%), 250 (14), 249 (60), 194 (29), 193 (100), 192 (60), and 165 (16), *m** 149 (249 ⟶ 193); the 5,14-*bischloroacetyl analogue* (16) (25%), m.p. 317—320° (Found: C, 71·4; H, 4·6; Cl, 12·9; N, 5·0. $C_{32}H_{24}Cl_2N_2O_2$ requires C, 71·2; H, 4·5; Cl, 13·1; N, 5·2%), $\nu_{max.}$ 1665 (C=O), 1500, 1298, 1265, 1140, 780, 765, 755, 740, and 700 cm^{-1}, *m/e* 542/540 (M^+, <1%/<1%), 503 (<1), 383 (1), 271/269 (14/42), 193 (28), 192 (100), 191 (16), 190 (10), 180 (12), and 165 (12), *m** 136·5 (271/269 ⟶ 192); the 5,14-*dibenzoyl analogue* (17) (30%), m.p. 300—304° (Found: C, 84·6; H, 5·1; N, 4·9. $C_{42}H_{30}N_2O_2$ requires C, 84·6; H, 5·0; N, 4·9%), $\nu_{max.}$ 1660 (C=O), 1500, 960, 780, 755, and 740 cm^{-1}, *m/e* 594 (M^+, <1%), 489 (M − COPh, <1), 298 (10), 297 (44), 193 (16), 192 (84), 191 (18), 182 (16), 165 (18), 106 (10), 105 ($PhCO^+$, 100), and 77 (44), *m** 124 (297 ⟶ 192) and 56·5 (105 ⟶ 77); the 5,14-*bisethoxycarbonyl analogue* (18) (30%), m.p. 325—327° (Found: C, 76·8; H, 5·8; N, 5·4. $C_{34}H_{30}N_2O_4$ requires C, 77·0; H, 5·7; N, 5·3%), $\nu_{max.}$ 1700br (C=O), 1495, 1395, 1340, 1225, 1200, 1100, 1085, 1050, 1030, 780, 760, 743, and 715 cm^{-1}, *m/e* 530 (M^+, <1%), 457 (M − OEt, <1), 266 (16), 265 (100), 193 (17), and 192 (76), *m** 139 (265 ⟶ 192); and the 5,14-*dicarbamoyl analogue* (99%), m.p. 367—370° (Found: C, 76·0; H, 5·1; N, 11·7. $C_{30}H_{24}N_4O_2$ requires C, 76·2; H, 5·1; N, 11·9%), $\nu_{max.}$ 1655 (C=O), 1645, 1590br, 1570, 1500, 775, 760, and 745 cm^{-1}, *m/e* 472 (M^+, <1%), 429 (M − HN=C=O, <1), 236 (22), 194 (20), 193 (100), and 180 (12), *m** 158 (236 ⟶ 193); and the *dimer* (24) (90%), m.p. 254° (Found: C, 82·4; H, 6·5; N, 5·1. $C_{78}H_{72}N_4O_4$ requires C, 82·6; H, 6·6; N, 5·1%), $\nu_{max.}$ 1665br (C=O), 1500, 1100br, 775, 760, and 720 cm^{-1}, *m/e* 1104 (M^+, <1%), 551 (<1), 361 (97), 360 (99), 194 (98), 193 (100), 192 (98), 191 (67), and 165 (45).

8-*Acetyl*-3a,3b,12b,12c-*tetrahydro*-3-*methyl*-3H,8H-*dibenzo*[b,f]*pyrrolo*[3′,4′:3,4]*cyclobut*[1,2-d]*azepine*-1,3-*dione* (20).—A solution of 5-acetyldibenzo[*b,f*]azepine (100 mg), *N*-methylmaleimide (100 mg), and benzophenone (200 mg) in acetone (14 ml) was purged with nitrogen for 0·5 h and then irradiated for 1 h. The solution was evaporated to dryness and the solid residue, recrystallised from petroleum (b.p. 40—60°)–ether (1 : 9 v/v), afforded the *adduct* (21 mg, 15%), m.p. 227—229° (Found: C, 73·0; H, 5·3; N, 8·2%; M^+, 346·1305. $C_{21}H_{18}N_2O_3$ requires C, 72·8; H, 5·2; N, 8·1%; M, 346·1317), $\nu_{max.}$ 1760 and 1690 (imide), 1665 (C=O), 1495, 1335, 1280, 1120, 960, 765, 760, and 740 cm^{-1}, τ 2·5—3·0 (8H, m, ArH), 6·05br (2H, CHCO), 6·3—6·9 (2H, ArCH), 6·93 (3H, s, NMe), and 7·08 (3H, s, Ac), *m/e* 346 (M^+, 30%), 304 (M − O=C=CH_2, 19), 235 (22), 194 (15), 193 (100), 192 (34), 180 (15), 165 (15), 137 (41), and 111 (15), *m** 267 (346 ⟶ 304).

Similarly prepared was the 11-*phenyl analogue* (21) (34 mg, 20%), m.p. 253—255° (from ether) (Found: C, 76·6; H, 5·1; N, 7·0%; M^+, 408·1469. $C_{26}H_{20}N_2O_3$ requires C, 76·5; H, 5·0; N, 6·9%; M, 408·1474), $\nu_{max.}$ 1770 and 1705 (imide), 1660 (C=O), 1500, 1185, 1155, 770, 765, 740, and 718 cm^{-1}, τ 2·4—2·9 (13H, m, ArH), 5·9br (2H, CHCO), 6·1—6·7 (2H, ArH), and 7·75 (3H, s, Ac), *m/e* 408 (M^+, 14%), 366 (M − O=C=CH_2, 6), 235 (26), 194 (17), 193 (100), 192 (32), and 180 (14), *m** 328 (408 ⟶ 366).

[29] G. Bender and G. Schultz, *Ber.*, 1886, **19**, 3237.

Irradiation of 5-p-*Tolylsulphonyldibenz*[b,f]*azepine*.—A solution of the sulphonamide (3·0 g) in benzene (50 ml) was irradiated for 1 h. The solution was evaporated and the resulting oil chromatographed on a column of neutral alumina (350 g) made up in petroleum. Elution with petroleum–benzene afforded starting material (2·0 g). Benzene–methanol (2 l; 9 : 1 v/v) eluted 2-p-*tolylsulphonyldibenz*[b,f]*azepine* (0·25 g) as red crystals, m.p. 230—231° [from benzene–methanol (3 : 1 v/v)] (Found: C, 72·8; H, 5·1; N, 3·9; S, 9·1. $C_{21}H_{17}NO_2S$ requires C, 72·6; H, 4·9; N, 4·0; S, 9·2%), $\nu_{max.}$ 3350 (NH), 1600br, 1320, 1305, 1160, 1130, 1100, 830, 815, 750, 705, and 670 cm^{-1}, *m/e* 347 (M^+, 100%), 348 (20), 193 (16), 192 ($M - SO_2C_6H_4Me$, 24), 191 (24), and 190 (12). G.l.c. analysis (silicone; 200°) of the solution showed no detosylation product.

5,10-*Diacetyldibenz*[b,f]*azepine*.—Acetyl chloride (1·4 g) in carbon dilsulphide (10 ml) was added dropwise to a stirred mixture of aluminium trichloride (5 g) and 5-acetyldibenz-[*b,f*]azepine (4·0 g) in carbon disulphide (100 ml), cooled in an ice–water bath. The mixture was stirred for 1 h at room temperature and then refluxed for 3 h. After cooling, the lower viscous layer was added with stirring to cracked ice. Filtration afforded the crude product, which was dried and recrystallised from ethanol–ether (4 : 1 v/v) to give 5,10-*diacetyldibenz*[b,f]*azepine* (2·6 g, 45%), m.p. 163—164° (Found: C, 77·8; H, 5·5; N, 5·2. $C_{18}H_{15}NO_2$ requires C, 78·0; H, 5·5; N, 5·1%), $\nu_{max.}$ 1665 (C=O), 1495, 1340, 1270, 1230, 900 (CH=CH<), and 665 cm^{-1}, *m/e* 277 (M^+, 45%), 278 ($M + 1$, 10), 236 (18), 235 ($M - C_2H_2O$, 100), 234 (M — COMe, 50), 192 (21), 191 (15), 190 (16), and 165 (16), *m** 199 (277 ⟶ 235). Similarly prepared were 10-*acetyl-5-propionyldibenz*[b,f]*azepine* (69%), m.p. 167—168° (from benzene) (Found: C, 78·2; H, 5·7; N, 4·7%; M^+, 291·1250. $C_{19}H_{17}NO_2$ requires C, 78·3; H, 5·9; N, 4·8%; M, 291·1259) $\nu_{max.}$ 1665br (C=O), 1500, 1305, 1295, 1230, 1085, 910, and 775 cm^{-1}, *m/e* 291 (M^+ 35%), 292 ($M + 1$, 7), 236 (19), 235 ($M - C_3H_4O$, 100), 234 (M — COEt, 41), 192 (11), 191 (11), 190 (13), and 165 (10), *m** 190 (291 ⟶ 235); and 10-*acetyl-5-chloroacetyldibenz*[b,f]*azepine* (55%) (as very pale yellow prisms), m.p. 172—174° (from methanol) (Found: C, 69·2; H, 4·6; Cl, 11·2; N, 4·7. $C_{18}H_{14}ClNO_2$ requires C, 69·3; H, 4·5; Cl, 11·4; N, 4·5%), $\nu_{max.}$ 1665 (C=O), 1500, 1310, 1270, 1235, 1130, 1005, 905, 765, and 750 cm^{-1}, *m/e* 313/311 (M^+, 7%/33%), 235 (18), 234 (M — $COCH_2Cl$, 100), 192 (7), 191 (6), 190 (6), and 165 (5), *m** *ca.* 176 (313/311 ⟶ 234).

Reaction of 5-*Methyldibenz*[b,f]*azepine with Acetyl Chloride–Aluminium Trichloride*.—Acetyl chloride (4·2 g) was added dropwise during 0·5 h to a stirred mixture of aluminium trichloride (10 g) and 5-methyldibenz[*b,f*]azepine (6·8 g) in carbon disulphide (50 ml), cooled in an ice–water bath. The mixture was stirred for 1 h at room temperature and then refluxed for 5 h. After cooling, the lower viscous layer was treated with ice–water, and the yellow product was filtered off and dried. This material was dissolved in hot methanol; the solution was filtered and evaporated and the residue recrystallised from methanol to afford starting material (5·9 g, 74%), m.p. 140—142° (lit.,[25] 143—144·5°). The aqueous filtrate was extracted with dichloromethane and the extract dried ($MgSO_4$) and evaporated. The resulting oil crystallised from methanol to give a product (100 mg) tentatively identified as 2,8-diacetyldibenz[*b,f*]azepin-10-(11*H*)-one (30), m.p. 238—240° (Found: M^+, 293·1048. $C_{18}H_{15}NO_3$ requires M, 293·1052), $\nu_{max.}$ 3500w (HO of enol form), 3300 (NH), 1660br (C=O), 1598, 1580, 1495, 1270, 1240br, 1170, 1120, 980, 960, 895, 830, and 720 cm^{-1}, τ 2·16 (1H, d, J_{meta} 3 Hz, ArH), 2·5—2·7 (5H, m, ArH), 7·34 (3H, s, Ac), 7·47 (2H, s, $COCH_2$), and 8·13 (3H, s, Ac). The low-field n.m.r. absorption was assigned to the highly de-shielded *meta*-coupled 9-proton, which has a chemical shift appropriate to an aromatic proton flanked by carbonyl groups (*cf.* pyromellitic anhydride, τ 2·05), *m/e* 293 (M^+, 53%), 294 ($M + 1$, 10), 279 (22), 278 (M — Me, 100), 250, (M — COMe, 4), 235 (M — COMe — Me, 22), 207 (M — 2COMe, 5), and 192 (5), *m** 264 (293 ⟶ 278) and 225 (278 ⟶ 250). A peak at 131·5 (*m/2e*) was assigned to the doubly charged ion resulting from the loss of two methyl groups from the molecular ion.

A similar reaction with nitrobenzene as solvent gave starting material (87%) after chromatography (neutral alumina) of the crude product.

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