The Synthesis and Chemistry of 4-Aza-azulene.[1]

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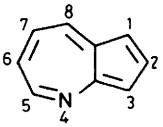
4-Aza-azulene and its 5-bromo and 6-methoxy derivatives have been efficiently synthesized by spray pyrolysis of 2-halogenoindan-1-yl azidoformates at 300 °C and 1—2 mm pressure of nitrogen. Bromination of 4-aza-azulene gives 1-bromo, 3-bromo, and 1,3-dibromo derivatives. Attempts to nitrate, trifluoroacetylate, or acetylate were unsuccessful. Diethyl azodicarboxylate gave a mixture of 1-and 3-hydrazinedicarboxylates, also probably by electrophilic substitution. Dimethyl acetylenedicarboxylate (DMAD) reacted by initial attack at nitrogen to give three adducts. The structures of two of these have been solved, one being a 3:1 adduct and the other the dimer of a 2:1 adduct of DMAD with aza-azulene. The latter was subjected to an *X*-ray crystallographic study. The action of *m*-chloroperbenzoic acid yielded the aza-azulene *N*-oxide.

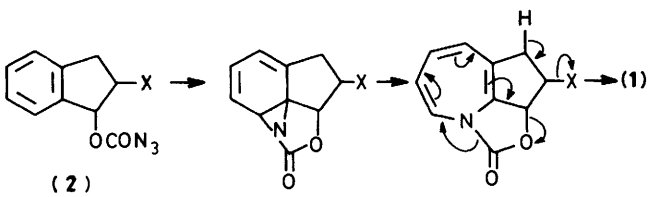
All the mono-aza-azulenes[2] are known in the form of their derivatives although only the parent 1-,[3] 5-,[4] and possibly 6-aza-azulene[5] have been prepared. The systems with nitrogen in the 5-membered ring are stable whereas their analogues bearing a 7-membered-ring nitrogen are unstable and elusive. The only example known of a 4-aza-azulene is the 1,2,3-triphenyl derivative prepared accidentally during the formation of a pyrrolidine enamine of a triphenylcyclopentenone.[6] Since these unstable aza-azulenes remain difficult to produce and virtually unexplored, we have embarked on a study of their ready synthesis and chemistry. This paper discloses our findings regarding the least studied isomer, 4-aza-azulene (**1**).



(**1**)

Nitrenes are well known for their ability to add to a benzenoid ring and thereby yield an azepine.[7] Amongst the most versatile and reactive of the family of nitrenes are those derived from azidoformates by thermolysis. These nitrenes (in their singlet state) readily add to alkenes and aromatics and insert stereospecifically into alkane C–H bonds.[7] We have demonstrated elsewhere that by conducting such reactions in the vapour phase, conveniently by use of 'spray pyrolysis',[8] high yields of the corresponding intramolecular reaction products ensue.[9] By constructing a suitable 6,5-fused azidoformate that could thereby yield a 7,5-fused product by such a ring expansion, an aza-azulene should be formed.

These requirements are adequately met by an indan-1-yl azidoformate (**2**), wherein the substituent X should (a) be capable of blocking attack of the nitrene at this alternative site of attack, and (b) be readily eliminable as HX to make for the correct oxidation level for aromatisation of the intermediate hydroaza-azulene (Scheme 1). A halogen atom should prove ideal for both of these purposes.

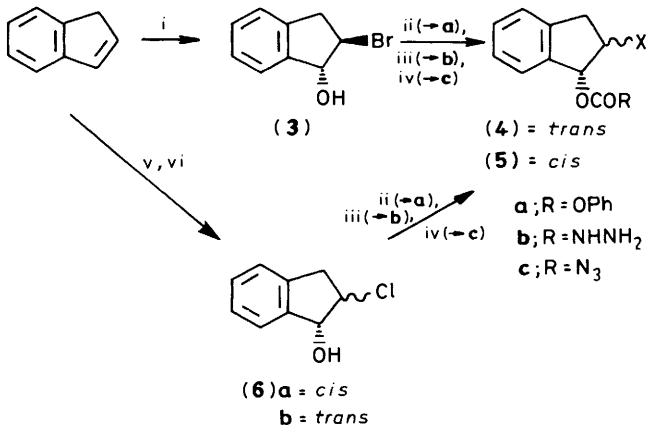


(**2**)

Scheme 1.

Early work was not encouraging; indan-1-yl azidoformate (**2**; X = H) gave no meaningful product on pyrolysis at 300 °C. However, the 2-halogenoindan-1-yl azidoformates (**2**; X = *cis*- or *trans*-Cl or -Br) proved spectacularly successful in that, irrespective of the nature of the halide or its stereochemistry, 4-aza-azulene (**1**) was produced directly and in good yield. Initial pyrolyses with an open 'hot tube' gave the product (**1**) but in poor yield probably due to the hydrogen halide eliminated. In order to remove the hydrogen halide we examined column packings to absorb this by-product. Copper turnings and calcium oxide chips were both effective and a combination of the two resulted in reproducible yields of the 4-aza-azulene of 80%, the method allowing several grams of product to be produced in one batch.

The indanyl azidoformates were readily generated in high overall yield by, for example (i) phase-transfer-catalysed addition of hypobromite to indene followed by treatment successively with phenyl chloroformate [to give (**4a**)], hydrazine hydrate [yielding (**4b**)], and nitrous acid to give, for example, the *trans*-2-bromo azide (**4c**; X = Br) in 37% overall yield based on indene; (ii) the addition of chlorine to indene followed by hydrolysis gave a mixture of *cis*- and *trans*-chlorohydrin (**6**) which were readily separated. These two routes are shown in Scheme 2.



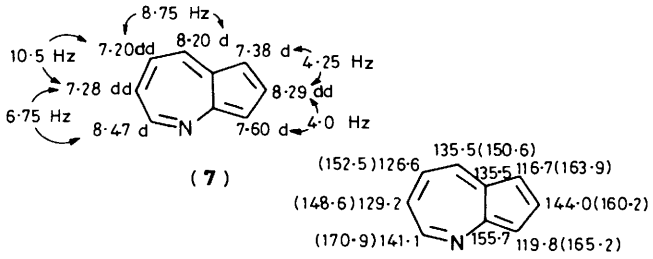
Scheme 2. *Reagents:* i, HOBr; ii, PhOCOCl; iii, NH_2NH_2; iv, $[HNO_2]$; v, Cl_2; vi, aqueous EtOH, heat

Treatment of the *cis*-chlorohydrin (**6a**) as above gave the *cis*-azidoformate (**5c**; X = Cl) in 50% yield (based on the chlorohydrin). The *trans*-chloro azidoformate (**4c**; X = Cl) was

similarly prepared in 45% yield. The *trans*-bromo azidoformate (**4c**; X = Br) is the most convenient starting material.

4-Aza-azulene (**1**) collects on the cold finger of the pyrolysis apparatus as deep turquoise crystals and is best washed off rapidly with dichloromethane and chromatographed on silica with the same solvent. It is stable in solution in the dark (being slowly decomposed in daylight) but rapidly decomposes in the free state in the presence of oxygen (but not under nitrogen). Chromatography yields a deep, royal blue solution which yields a dark turquoise liquid on evaporation under nitrogen. It is best stored in solution in a refrigerator where it can be kept for several months. It is soluble and stable in dilute mineral acids and has a quinoline-like odour. 4-Aza-azulene may also be formed by addition of the azide (**2**) to refluxing 1,1,2,2-tetrachloroethane followed by rapid cooling, though the yields are very low due to thermal decomposition of the product.

4-Aza-azulene showed a first-order ^{1}H n.m.r. spectrum at 500 MHz ($CDCl_3$) and with the aid of decoupling showed shifts and couplings as in structure (**7**). These results compare favourably with those of the 1,2,3-triphenyl derivative[6] which showed protons 5-, 6-, 7-, and 8-H at δ_H 8.26, 7.10, 7.01, and 7.97 respectively and $J_{5,6}$, $J_{6,7}$, and $J_{7,8}$ values of 6.5, 9.5, and 9.0 Hz respectively. The ^{13}C n.m.r. shifts are shown in structure (**8**) with $^1J_{C,H}$ data in parentheses.

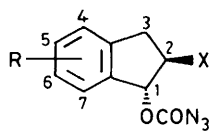


(**7**)

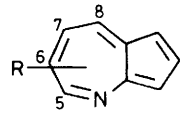
(**8**)

The u.v. spectrum of this aza-azulene compares favourably with that of azulene itself and with that of 5-aza-azulene[4] (Figure 1). In its mass spectrum the molecular ion is the base peak and shows successive loss of HCN and acetylene. The molecular ion gives an appropriate accurate mass measurement.

The pyrolysis of substituted *trans*-2-bromoindan-1-yl azidoformates (**9**) was next studied. Interestingly, the dibromo-azidoformate (**9a**) gave solely 7-bromoazulene (**10a**) in 30% yield as an unstable green crystalline solid (giving a royal blue solution) with no evidence of loss of the aryl bromide. However, when 5-bromoindan-1-yl azidoformate (**9c**) was pyrolysed, 4-aza-azulene (**1**) itself was formed though in only 10% yield, showing that while this bromide is capable of elimination after suitable H-shifts, it is decidedly a more energetic process. A similar pyrolysis of the 6-methoxyindanyl azidoformate (**9b**) gave 6-methoxy-4-aza-azulene (**10b**) as a dark purple oil (in 50% yield). Much to our disappointment, the electron-releasing methoxy group did not stabilise the aza-azulene system; indeed the product was even more prone to oxidative degradation than the parent system.



	R	X
(**9**) **a**;	5-Br	Br
b;	6-OMe	Br
c;	5-Br	H



(**10**) **a**; R = 7-Br
b; R = 6-OMe

We next examined the chemistry of 4-aza-azulene. While addition of elemental bromine in chloroform signalled the immediate loss of the blue colour with no meaningful product formation, use of *N*-bromosuccinimide (NBS) in a 1:1 mixture of dichloromethane and acetic acid proved highly effective for electrophilic substitution of the azulene. Addition of small aliquots of the solid reagent caused instant reaction; the formation of products and disappearance of the starting material were readily followed by t.l.c. (silica gel; dichloromethane: the more bromine atoms incorporated the more mobile was the product). When about an equimolar amount of the reagent had been added a readily separated mixture of green 1-bromo- (60%), 3-bromo- (7%), and 1,3-dibromo-4-aza-azulene (25%) was isolated together with a little starting material. Addition of further reagent (2.3 equiv. in all) led to more of the 1,3-dibromo-derivative (68%) at the expense of the other products, with no evidence of further substitution in the 7-membered ring. The substitution pattern is analogous to that of azulene itself.[10] The 1-bromo derivative is extremely unstable even in solution, while the 3-isomer is less stable than the parent (**1**). However, the 1,3-dibromo derivative is a relatively stable, green crystalline solid, surviving even in air for a day. It reacts vigorously with morpholine or piperidine at 0 °C in dichloromethane giving the base hydrobromide but no other meaningful product.

Other 'classical' electrophilic substitutions were less successful. Thus attempted nitration [copper(II) nitrate in acetic anhydride or tetranitromethane—both reagents known to nitrate azulene[10,11]] consumed starting material but gave no isolable product. Acetylation attempts with acetic anhydride–boron trifluoride–diethyl ether in dichloromethane were ineffective, the starting azulene being recovered. The action of trifluoroacetic anhydride in dichloromethane apparently gave an *N*-trifluoroacetylaza-azulenium trifluoroacetate in that t.l.c. gave a blue spot which remained on the base line but which upon column chromatography (silica:chloroform) yielded solely starting material. Attempts to isolate the salt by evaporation gave tarry material.

Attempts to add butyl-lithium in ether at 0 °C gave only tarry material.

Cycloaddition reactions were next examined. As with the isomeric quinoline system, aza-azulenes are known to react with dimethyl acetylenedicarboxylate (DMAD) by initial Michael addition of the ring nitrogen to the alkyne bond.[12] Thus

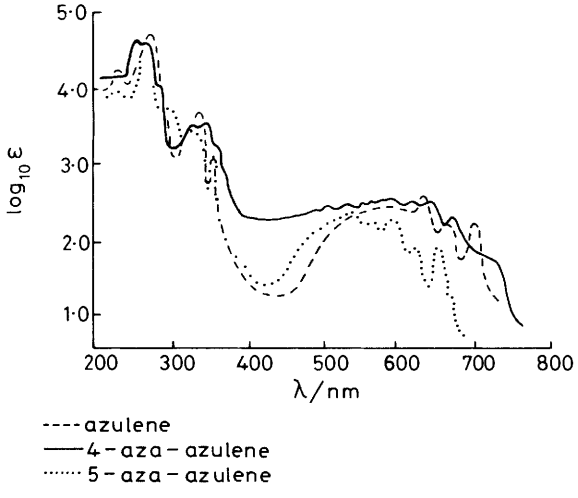
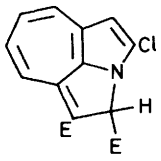
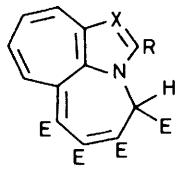


Figure 1. U.v. spectra of azulene and 4- and 5-aza-azulene

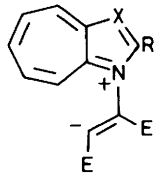
2-chloro-1-aza-azulene yields 1:1 and 1:2 adducts (**11**) and (**12a**), while 1,3-diaza-azulene rapidly gives a diadduct (**12b**), both pathways rationalised by way of the dipolar intermediate (**13**).[13a] The only cycloadditions to an isoquinoline isomer appear to be those of 6-phenyl-5-aza-azulene which gives a 1:2 adduct related to compound (**12**) at 80 °C but reveals true cycloaddition products at 160 °C.[13b,c] 4-Aza-azulene reacted at ambient temperatures with an excess of DMAD in dichloro-



(**11**)

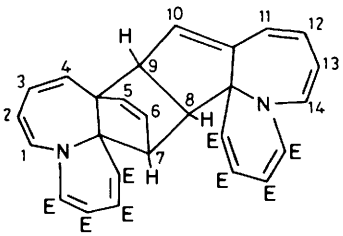


(**12**)a; X = CH, R = Cl
b; X = N, R = H

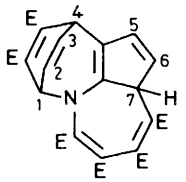


(**13**)

methane. After being kept for 9 days in the dark, the mixture gave three major products which were readily separated by medium-pressure chromatography. The least mobile product was obtained as red crystals, m.p. 195—196 °C, and proved to be a dimeric 1:2 adduct (**14**) while the more mobile product, a yellow oil, was a 1:3 adduct (**15**). The instability of the third and most mobile product, a purple oil, has hampered a structural assignment though evidence suggests that it could be another dimeric product.



(**14**)



(**15**)

E = CO_2Me

Non-systematic numbering schemes

The structural assignment of the dimer (**14**) stemmed particularly from the 500 MHz ^1H n.m.r. spectrum wherein it was evident that two similar but isolated groups of –CH=CH–CH=CH– units characteristic of an azepine were present, together with another chain of six CHs (*viz.* –CH=CH–CH–CH–CH–CH=). The structure was further corroborated by the presence of 8 carbonyl absorptions, 9 quaternary ethylenic carbons, 3 quaternary aliphatic carbons, 11 ethylenic CHs, 3 aliphatic CHs, and 8 methyl absorptions in the ^{13}C n.m.r. spectrum (see Experimental section for full details). Not surprisingly the mass spectrum revealed a molecular ion (*m/z* 413) of half the true mass. The structure was finally put beyond doubt by an *X*-ray crystallographic study.

For the *X*-ray structure determination the atomic numbering scheme for the molecule as shown in the perspective drawing (Figure 2) was used. Hydrogen atoms are numbered according to the numbers of the atoms to which they are attached.

In order to identify the conformation of the five-, six-, and seven-membered rings in the system, their puckering parameters were calculated as described by Cremer and Pople,[14] and these conformations are described with the aid of defined[15] nomenclature (Table 1). The severe puckering of the D-ring is evident from the large value for *Q* (0.94).

Table 1. Puckering parameters for the dimer (**14**)

Ring atoms	θ	φ	*Q*	Conformation[a]
8A, 8B, 17B, 18, 18A		141.0	0.63	^5E
8A. 20, 19, 18, 18A		323.9	0.57	$_5E$
8B, 9, 9A, 17A, 17B		322.2	0.09	planar
N4A, 18A, 1, 2, 3, 4	113.0	218.9	0.52	$^2S_1$
N13A, 14, 15, 16, 17, 17A	72.1	307.7	0.58	$E_6 + B_{3,6}$
8A, 8B, 17B, 18, 19, 20	88.7	1.8	0.94	$^{1,4}B$
N4A, 5, 6, 7, 8, 8A, 18A		φ(2) 237.5	0.39	*TS*3 + *TB*3
		φ(3) 327.5	0.32	
N13A, 17A, 9A, 10, 11, 12,		φ(2) 326.9	0.60	*S*3
13,		φ(3) 225.9	0.19	

[a] The numerical position of a ring atom in the sequences of the first column is used as an identifier in the conformational symbols of the last column.

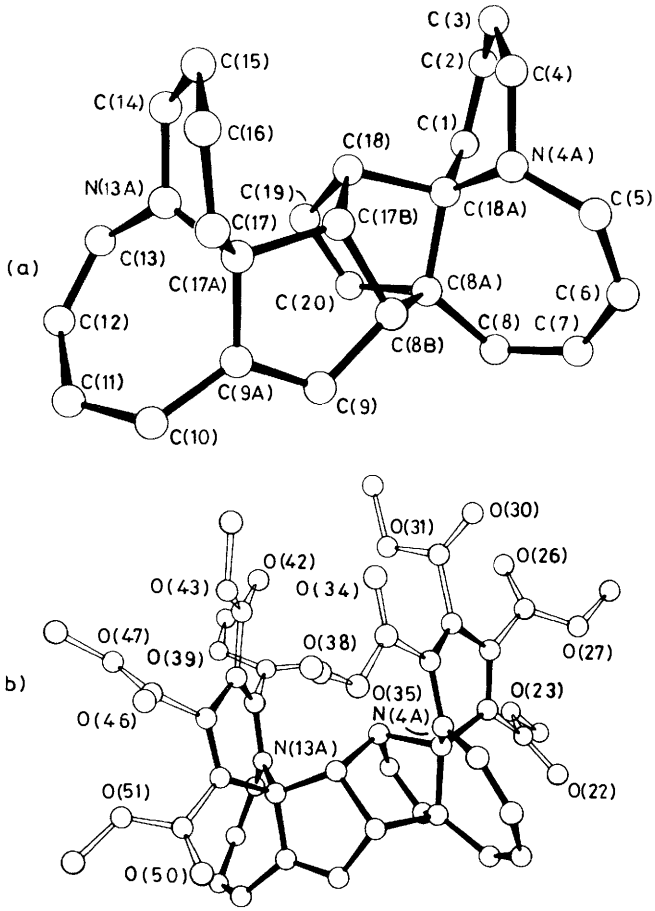
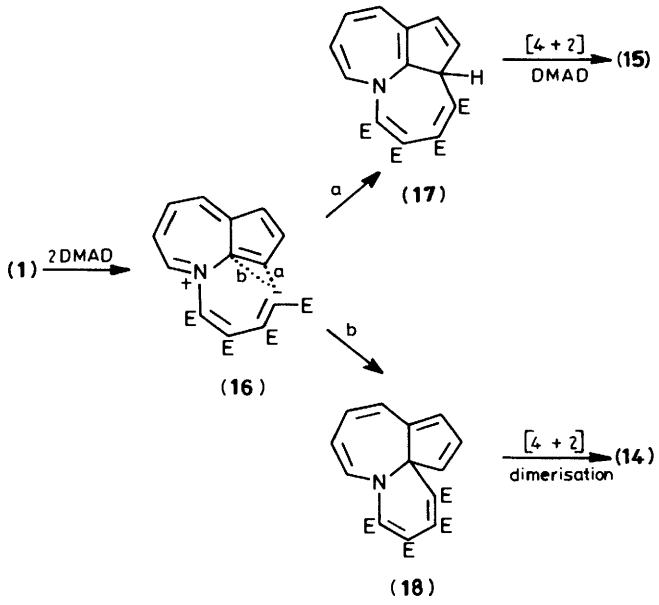


Figure 2. Perspective drawings of the dimer (**14**). (a) Crystallographic numbering scheme; methoxycarbonyl groups deleted for clarity, (b) crystallographic numbering scheme of the methoxycarbonyl groups

The second adduct proved less problematic and revealed a mass spectral molecular ion (*m/z* 555) indicative of a 1:3 adduct. The ^1H n.m.r. spectrum, even at 90 MHz, was readily resolved and strongly supported the structure (**15**) since it revealed, by means of decoupling studies, 7 CHs (3 aliphatic and 4 olefinic multiplets) with appropriate connectivity. Again, the ^{13}C n.m.r. data proved definitive.

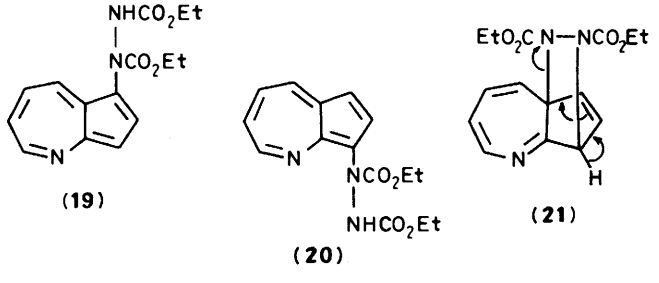


Scheme 3.

We explain these reactions, by analogy to the literature, as shown in Scheme 3.

The dipolar intermediate (**16**) from attack of two molecules of DMAD on the aza-azulene nitrogen has several alternative sites available for ring-closure. Of these routes (a) and (b) are the most favoured and by further Diels–Alder addition of DMAD to the 1*H*-azepine ring of compound (**17**) in a well established manner,[16] the product (**15**) is derived. Route (b) leads to a fused cyclopentadiene (**18**) apparently conveniently set up for a ready [4 + 2] dimerisation to give dimer (**14**). Support for the rate-determining involvement of the dipolar intermediate (**16**) derives from the solvent dependence of the reaction. In acetonitrile solution the same products derive in lower yields but the reaction was complete in 24 h.

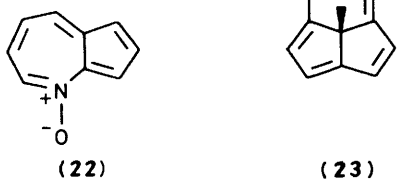
Diethyl azodicarboxylate (DEAD) was next utilised and in dichloromethane solution the reaction was complete in 6 days. T.l.c. studies revealed only one blue product as well as formation of diethyl hydrazine-1,2-dicarboxylate. Medium-pressure liquid chromatography, however, separated two blue isomers, both being azulene chromophores and derived by 1:1 interaction of the reactants. They were readily assigned the structures (**19**) and (**20**) formed in the ratio 3:1 and in a combined 30% yield.



While it could be argued that these products derive from [4 + 2] cycloaddition of DEAD to the five-membered ring of the aza-azulene in the two possible modes followed by ring-opening of the adduct [*e.g.*, (**21**) would yield (**20**)], electrophilic substitution would seem a better explanation. DEAD is known to be an efficient electrophile and substitutes cyclazines, for example in a similar manner to that described above.[17] The sites and site-specificity of substitution are as for bromination.

To our surprise, other dienophiles were either without effect [maleic anhydride, diethyl maleate, furan, 2,3-dihydropyran, ethyl acrylate, acrylonitrile and bis(trimethylsilyl)acetylene] or reacted with formation of tar (tetracyanoethylene, ethyl propiolate, and chlorosulphonyl isocyanate).

4-Aza-azulene (**1**) reacted readily at room temperature with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane solution to give the green crystalline *N*-oxide (**22**) as a moderately stable product. This product, unlike the isomeric quinoline *N*-oxide, was stable to extended u.v. irradiation and to the action of toluene-*p*-sulphonyl chloride in pyridine. 1,3-Dibromo-4-aza-azulene did not react with MCPBA under the same conditions.



Seeking a stable, storable solid derivative we examined charge-transfer complexes. Trinitrobenzene in benzene did not yield a precipitate or reveal any other product by t.l.c. However, evaporation of the solvent gave a dark crystalline mass which was reasonably stable in air for a period of three months. Addition of solvent regenerated the two components.

Similarly with tetranitrofluorenylidenemalononitrile (TNFM), known to form a charge-transfer complex with the annulene (**23**),[18] a black crystalline residue formed from equimolar amounts of (**1**) and TNFM in CH_2Cl_2 although the regeneration of (**1**) by addition of solvent appears to be less efficient.

Experimental

M.p.s were recorded on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were obtained on a Perkin-Elmer 257 spectrophotometer and ^1H n.m.r. spectra on a Varian EM390 or Bruker WM500 spectrometer operating at 90 or 500 MHz respectively. The n.m.r. data refer to deuteriochloroform solutions relative to tetramethylsilane as internal standard. ^{13}C N.m.r. (125 MHz) spectra were recorded on the Bruker WM500 spectrometer for deuteriochloroform solutions. Mass spectra were taken on a Varian MAT 212 instrument and *X*-ray crystallographic studies were performed on a Philips PW 1100 full-circle diffractometer. Chromatography utilised silica thoughout; t.l.c. plates were Merck Silica Gel 60 F-254 while for column chromatography Merck Silica Gel 60 (70—230 mesh) was used. The medium-pressure liquid chromatography system used a column (94 cm × 1.6 cm) packed with silica gel (0.032—0.063 nm) from ICN Pharmaceuticals, Cleveland, U.S.A. Light petroleum refers to that fraction with b.p. 60—80 °C. The spray pyrolysis apparatus has already been described in detail[8] and was operated at *ca.* 300 °C and under 1—2 mm pressure of nitrogen.

Preparation of Indan-1-ols.—(a) *Indan-1-ol.* The title compound was prepared by the method of Weissgerber,[19] m.p. 51—52 °C (lit.,[19] 54 °C).

(b) 2-*Chloroindan-1-ol.* The method described by Suter and Lutz[20] afforded both *cis*-2-chloroindan-1-ol (**6a**), m.p.

110.5—111.5 °C (lit.,[20] 110—111 °C) and *trans*-2-chloroindan-1-ol (**6b**), m.p. 124 °C (lit.,[20] 123—124 °C).

(c) trans-2-*Bromoindan*-1-*ol* (**3**). This method was a modification of that described by Suter and Milne.[21] Indene (55 ml, 0.42 mol) was suspended in vigorously stirred water (150 ml) and a small amount of phase-transfer catalyst, triethylbenzylammonium chloride, was added. To a solution of potassium bromide (53 g, 0.45 mol) in water (100 ml) was added bromine (23 ml, 0.45 mol), and the mixture was added slowly to the indene suspension. After the addition the mixture was stirred at 50 °C until the colour due to the bromine solution had dissipated. After having cooled, the resulting white pasty mass was filtered under suction and recrystallised to give the title compound (70 g, 73%), m.p. 128—129 °C (from ethanol) (lit.,[21] 126—127 °C).

(d) 5-*Bromoindan*-1-*ol*. The procedure described by Quere and Maréchal[22] was utilised to give 5-bromoindanone, m.p. 124—125 °C (from light petroleum) (lit.,[22] 126—127 °C). 5-Bromoindanone (11.0 g, 0.052 mol) in ethanol (50 ml) was reduced with sodium borohydride (1.0 g, 0.026 mol). After being stirred overnight, the resulting solution was poured into water and extracted with ether. The extract was dried ($MgSO_4$) and evaporated to give 5-bromoindanol as a brown solid which recrystallised from light petroleum as white needles (10.0 g, 90%), m.p. 78—79 °C (lit.,[22] 79—80 °C).

(e) 2,5-*Dibromoindan*-1-*ol*. 5-Bromoindanol (7.8 g, 0.037 mol) was refluxed in benzene (100 ml) in the presence of toluene-*p*-sulphonic acid for 30 min. The benzene solution was cooled and washed thoroughly with water. Evaporation of the benzene gave a red oil which was distilled using a Kugelrohr apparatus (oven temperature 50 °C) to give 6-bromoindene as a white solid (4.7 g, 66%), m.p. 26—28 °C (lit.,[22] b.p. 50 °C/0.1 mmHg).

The method of Dalton *et al.*[23] was utilised for the preparation of the bromohydrin from 6-bromoindene, whereby 6-bromoindene (4.7 g, 0.024 mol) was dissolved in a mixture of dimethyl sulphoxide (50 ml) and water (1 ml) and the solution was cooled to below 10 °C. Under N_2, NBS (8.5 g, 0.048 mol) was added in one portion. A suspension formed and the mixture was stirred for 1.5 h. The resulting orange solution was poured into water and extracted with ether. The extract was washed successively with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated to give a white solid which was recrystallised from ethyl acetate–light petroleum to give trans-2,5-*dibromoindan*-1-*ol* as water-white needles (5.3 g, 75%), m.p. 136 °C (Found: C, 36.5; H, 2.7; Br, 54.0. $C_9H_8Br_2O$ requires C, 36.9; H, 2.7; Br, 54.7%); $\nu_{max.}$(Nujol) 3 290 cm^{-1} (OH); δ_H (90 MHz; $CDCl_3$) 2.4 (1 H, br s, OH), 3.2 (1 H, dd, *J* 16.5 and 7 Hz, 3-H_a), 3.6 (1 H, dd, *J* 6 Hz, 3-H_b), 4.25 (1 H, q, 2-H), 5.25 (1 H, d, *J* 3 Hz, 1-H), and 7.33 (3 H, m, ArH).

(f) 2-*Bromo*-6-*methoxyindan*-1-*ol*. 6-Methoxyindan-1-one was prepared according to the method described by House and Hudson.[24] Bromination of the ketone was carried out using the method of King and Ostrum.[25] To a refluxing suspension of $CuBr_2$ (27.5 g, 0.12 mol) in ethyl acetate (50 ml) was added dropwise a solution of 6-methoxyindan-1-one (10 g, 0.06 mol) in chloroform (50 ml) during 15 min. The dark green mixture gave way to a white solid suspended in a light green solution. The solution was refluxed for 1 h. The solid was filtered off and washed with chloroform. The combined chloroform extracts were concentrated. Chromatography on silica [light petroleum–$CHCl_3$ (9:1)] gave 2-bromo-6-methoxyindan-1-one as a white solid (11.0 g, 75%), m.p. 107—108 °C; $\nu_{max.}$(Nujol) 1 700 cm^{-1} (CO); δ_H (90 MHz; $CDCl_3$) 3.27 (1 H, dd, *J* 17.3 and 3 Hz, 3-H_a), 3.73 (1 H, dd, *J* 7 Hz, 3-H_b), 3.83 (3 H, s, CH_3O), 4.65 (1 H, dd, 2-H), and 7.25 (3 H, m, ArH).

To a solution of 2-bromo-6-methoxyindan-1-one (10.0 g, 0.041 mol) in ethanol (50 ml) was added sodium borohydride (0.9 g, 0.023 mol) in portions. The orange solution became yellow in colour and this was followed by precipitation of a white solid. The mixture was stirred for 15 min and poured into water and extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated to give a white solid. Chromatography (CH_2Cl_2 as eluant) yielded cis-2-*bromo*-6-*methoxyindan*-1-*ol* as a white solid (7.1 g, 70%), m.p. 115—116 °C (Found: C, 49.4; H, 4.5; Br, 32.1. $C_{10}H_{11}BrO_2$ requires C, 49.4; H, 4.6; Br, 32.9%); $\nu_{max.}$(Nujol) 3 300 cm^{-1} (OH); δ_H (90 MHz; $CDCl_3$) 2.33 (1 H, br s, OH), 3.30 (2 H, br d, *J* 3 Hz, 3-H_2), 3.80 (3 H, s, CH_3O), 4.90 (2 H, dd, *J* 3.5 and 2 Hz, 1- and 2-H), and 7.00 (3 H, m, ArH).

Preparation of Indan-1-*yl Azidoformates*.—The general procedure, outlined for the preparation of indan-1-yl azidoformate, is as follows. Indan-1-ol (5.0 g, 0.037 mol) was dissolved in pyridine (5 ml) in a round-bottomed flask immersed in a water-bath. Phenyl chloroformate (5.8 ml, 0.047 mol) was added slowly to the stirred solution, and care was taken so that the temperature did not rise above 35 °C. On addition of the phenyl chloroformate a precipitate formed. The mixture was stirred at room temperature overnight and was then poured into water and the mixture was extracted with ether. The extract was washed successively with aqueous citric acid (10%), aqueous sodium hydrogen carbonate, and finally water. The ethereal extract was dried ($MgSO_4$) and evaporated to give indan-1-yl phenyl carbonate as an oil (**4**/**5a**; X = H) (8.9 g, 94%), $\nu_{max.}$ (liquid film) 1 750 (CO) and 1 230 cm^{-1} (C–O–C); δ_H (90 MHz; $CDCl_3$) 2.30 (2 H, m, 3-CH_2), 2.90 (2 H, m, 2-CH_2), and 6.10 (1 H, dd, *J* 3.6 and 3.9, 1-H); *m/z* 254 (M^+) 203, 162, 133, and 116.

To a solution of indan-1-yl phenyl carbonate (8.0 g, 0.004 mol) in ethanol (50 ml) was added hydrazine hydrate (2 ml, 0.034 mol) and the solution was stirred at room temperature for 2 h. The solution was then poured into cold water and extracted with chloroform. The extract was washed successively with aqueous sodium hydroxide and water. dried ($MgSO_4$), and evaporated to give indan-1-yl carbazate (**4**/**5b**; X = H) as a white solid (5.3 g, 88%), m.p. 90—91.5 °C, $\nu_{max.}$(Nujol) 3 410 (NH) and 1 685 (CO) cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.30 (2 H, m, 3-CH_2), 2.90 (2 H, m, 2-CH_2), 3.80 (2 H, br s, NH_2), 6.15 (1 H, dd, *J* 4 and 4.2 Hz, 1-H), 6.30 (1 H, br s, NH), and 7.15—7.50 (4 H, m, ArH). The crude carbazate was used without further purification.

The crude indan-1-yl carbazate (5.0 g, 0.026 mol) was dissolved in a mixture of acetic acid (20 ml) and water (15 ml) and the solution was cooled below 5 °C, stirred and treated dropwise with sodium nitrite (1.85 g, 0.027 mol) in water (5 ml), and the temperature was maintained below 5 °C. On addition of the aqueous sodium nitrite, a yellow solid precipitated out of solution. After the addition was complete, the mixture was stirred for 15 min at below 5 °C and for a further 1 h at room temperature. The resulting mixture was poured into water and extracted with ether. The extract was washed successively with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated. Chromatography on silica gel with light petroleum as eluant yielded *indan*-1-*yl azidoformate* (**4**/**5c**; X = H) as an oil (4.3 g, 93%); $\nu_{max.}$ 2 185, 2 140 (N_3) and 1 725 cm^{-1} (CO); δ_H (90 MHz; $CDCl_3$) 2.30 (2 H, m, 3-CH_2), 2.90 (2 H, m, 2-CH_2), 6.12 (1 H, dd, *J* 3.4 and 3.6 Hz, 1-H), 7.2—7.5 (4 H, m, ArH); *m/z* 203.0684 (M^+) ($C_{10}H_9N_3O_2$ requires *M*, 203.0693).

In a similar way the azidoformates in Table 2 were synthesised.*

* It was usual to filter off the solid carbazate and use this crude product in the next stage of the synthesis. Treatment of the crude product with base led to poor recovery and in some cases total loss of carbazate.

Table 2. Data for substituted indan-1-yl azidoformates (**4c**) and (**5c**)

Azidoformate			δ (multiplicity, *J*/Hz)						Found (%) (Required)		
	X	M.p. (° C)	1-H	2-H	3b-H	3a-H	Aromatic	$\nu_{max.}$(cm^{-1})	C	H	N
(**4c**)	Cl	39—40.5	6.21 (d, 3)	4.57 (ddd, 7, 4, 3)	3.65 (dd, 17, 4)	3.20 (dd, 17, 7)	7.3	2 170, 2 120, 1 720	50.5 (50.5)	3.3 (3.4)	17.6 (17.6)
(**5c**)	Cl	65—66	6.05 (d, 5)	4.75 (ddd, 6, 6, 5)	3.35 (d, 6)		7.3	2 190, 1 140, 1 725	50.5 (50.5)	3.8 (3.4)	17.4 (17.6)
(**4c**)	Br	36—37	6.25 (d, 3)	4.47 (ddd, 7, 4, 3)	3.65 (dd, 17, 4)	3.20 (dd, 17, 7)	7.3	2 180, 2 140, 1 725	42.9 (42.6)	2.95 (2.8)	13.9 (14.8)
(**9c**)		Oil	6.10 (dd, 7, 3)	2.9 (m) and 2.3 (m)			7.3	2 180, 2 130, 1 710	M^+, 282.9792. $C_{10}H_8BrN_3O_2$ requires *M*, 282.9778		
(**9a**)		Oil	6.19 (d, 3)	4.53 (ddd, 7, 4, 3)	3.65 (dd, 17, 4)	3.18 (dd, 17, 7)	7.4	2 180, 2 130, 1 720	M^+, 358.8904. $C_{10}H_7Br_2N_3O_2$ requires *M*, 358.8906		
(**9b**)		Oil	5.85 (d, 5)	4.75 (ddd, 6, 6, 5)	3.33 (br d, 6)		7.0	2 180, 2 140, 1 720	M^+, 310.9903. $C_{11}H_{10}BrN_3O_3$ requires *M*, 310.9906		

Table 3. ^{1}H and ^{13}C n.m.r. data for 4-aza-azulene (**1**) and its derivatives

Aza-azulene and substituent	δ_H						
	1-H	2-H	3-H	5-H	6-H	7-H	8-H
None (**1**)	7.38 (d, 4.3)	8.29 (dd, 4.3, 4.0)	7.60 (d, 4.0)	8.47 (d, 6.8)	7.28 (dd, 10.5, 6.8)	7.20 (d, 8.8)	8.20 (d)
7-Bromo (**10a**)	7.60 (m)	8.33 (dd, 4.2, 3.8)	7.30 (br d, 3.8)	8.15 (d, 7.5)	7.66 (d, 7.5)		8.43 (d, 3.5)
6-Methoxy (**10b**)	7.17 (br d, 4.3)	7.86 (dd, 4.3, 3.4)	7.50 (br d, 3.4)	8.30 (d, 3.0)		6.45 (dd. 9.8, 3.0)	7.89 (d, 9.8)
1-Bromo		8.30 (d, 4.3)	7.58 (d, 4.3)	8.52 (d, 3.0)	7.35 (m)		8.36 (m)
3-Bromo	7.26 (d, 4.6)	8.21 (d, 4.6)		8.57 (d, 6.4)	7.34 (m)		8.13 (d, 8.5)
1,3-Dibromo		8.15 (s)		8.55 (m)	7.35 (m)		8.10 (m)
N-Oxide	7.17 (dd, 4.0, 1.8)	7.75 (dd, 4.0, 4.0)	7.69 (dd, 4.0, 1.8)	8.16 (m)	7.04 (m)		8.16 (m)
1,2,3-Triphenyl[6]				8.26	7.10	7.01	7.97

	δ_C (p.p.m.) ($^1J_{CH}$)								
	C-1	C-2	C-3	C-3a	C-5	C-6	C-7	C-8	C-8a
None (**1**)	116.7 (163.9)	141.1 (160.2)	119.8 (165.2)	153.7	144.0 (170.9)	129.2 (148.6)	126.6 (152.5)	135.5 (150.6)	135.5
7-Bromo (**10a**)	117.0 (165.7)	139.2 (179.5)	120.7 (175.6)	155.6	146.0 (165.3)	131.8 (160.7)	122.4	138.5 (163.3)	132.5
6-Methoxy (**10b**)	108.2 (155.7)	135.2 (180.3)	117.4 (167.4)	149.3	137.2 (161.5)	160.1	120.6 (170.5)	134.4 (155.3)	131.5
1-Bromo	104.5	141.5	119.0	155.3	144.7	130.4	126.8	135.8	131.4
3-Bromo	115.8	142.3	107.7	148.9	144.1	130.9	127.9	136.4	135.8
1,3-Dibromo	103.3	142.3 (180.0)	106.4	149.0	144.3 (177.0)	131.9 (157.0)	127.7 (161.2)	136.5 (157.5)	132.1
N-Oxide	113.9 (176.9)	137.2 (162.4)	119.6 (173.0)	144.5	138.3 (168.6)	123.4 (158.3)	121.5 (165.2)	135.2 (171.4)	131.8
1,2,3-Triphenyl[6]									

Spray Pyrolysis of Azidoformates.—The azidoformates were decomposed using the technique of spray pyrolysis. The general procedure, outlined for 2-bromoindan-1-yl azidoformate (**4**/**5c**; X = Br), is as follows. *trans*-2-Bromoindan-1-yl azidoformate (**4c**; X = Br) (3.00 g) was spray-pyrolysed (300 °C/1 mmHg) at a rate of 0.5—1 g h^{-1}. The furnace was packed with a mixture of copper turnings and calcium oxide (3—8 mesh). A turquoise crystalline product collected on the cold finger. The product was obtained by removal of the cold finger from the apparatus and immediate dissolution of the product in CH_2Cl_2. This solution, including some condensed moisture, was chromatographed directly using CH_2Cl_2 as eluant to give firstly a small amount of starting azide (0.15 g, 5% recovery) followed by a dark blue solution. The majority of the solvent was removed under reduced pressure whilst the remaining traces of solvent were blown off under nitrogen to give 4-*aza-azulene* (**1**) (1.09 g, 80%) as a dark turquoise oil, *m*/*z* 129.0570 (M^+) (C_9H_7N requires *M*, 129.580). Similarly, the spray pyrolysis of 2,5-dibromoindan-1-yl azidoformate (**9a**) gave 7-*bromo*-4-*aza-azulene* (**10a**) as a dark blue oil (30%), *m*/*z* 206.9684 (M^+) (C_9H_6BrN requires *M*, 206.9684), and that of 2-bromo-6-methoxyindan-1-yl azidoformate (**9b**) gave 6-*methoxy*-4-*aza-azulene* (**10b**) as a dark purple oil (50%), *m*/*z* 159.0685 (M^+) ($C_{10}H_9NO$ requires *M*, 159.0684). The n.m.r. data for these substituted aza-azulenes, together with the data for other aza-azulenes prepared, are given in Table 3.

Table 4. ^{1}H N.m.r. data of adduct (**15**)

H	δ_H (multiplicity)	$J_{H,H}$ (Hz)
1	5.13 (dd)	5.6, 1.7
2	5.91 (dd)	10.2, 5.6
3	5.74 (ddd)	10.2, 6.1, 1.7
4	5.18 (d)	6.1
5	6.68 (br d)	5.3, 0.7
6	7.09 (dd)	5.3. 3.4
7	4.20 (br d)	3.4, 0.7

Table 5. ^{13}C N.m.r. data of adduct (**15**)

Carbon		δ_C (p.p.m.)
Quaternary carbons		175.2, 167.2, 163.9, 163.8, 163.4, 162.4, 162.3, 155.3, 149.9, 148.6, 138.1, 111.5, 100.7, 85.8
Methines	C_{sp^2}	146.3, 136.6, 134.0, 126.7
	C_{sp^3}	99.9, 56.2, 53.1
Methyls		53.1, 52.5, 52.3, 52.2, 52.2, 52.0

Solution Thermolysis of Azidoformates.—*trans*-2-Bromoindan-1-yl azidoformate (**4c**; X = Br) (1.0 g) in 1,1,2,2-tetrachloroethane (1 ml) was added rapidly to refluxing 1,1,2,2-tetrachloroethane (25 ml). The solution immediately became blue in colour. The heat source was removed and an ice-bath was applied. When the solution was cool it was poured directly onto a column and eluted with CH_2Cl_2. Only a trace of 4-aza-azulene (**1**) (<2%) was obtained.

Bromination of 4-Aza-azulene (**1**) *with NBS.*—To a solution of 4-aza-azulene (**1**) (0.17 g, 1.32 mmol) in CH_2Cl_2 (50 ml) and acetic acid (50 ml) was added NBS (0.24 g, 1.35 mmol) in one portion and the resulting solution was stirred at room temperature for 20 min. The solution was then poured into water (100 ml) and the organic layer was separated, washed well with water (3 × 100 ml), dried ($MgSO_4$), and concentrated. Chromatography using CH_2Cl_2 as eluant gave 1,3-*dibromo*-4-*aza-azulene* [51 mg, 25% based on (**1**) consumed] as an unstable green crystalline solid, m.p. 104 °C (decomp.); *m/z* 284.8788 (M^+) ($C_9H_5Br_2N$ requires *M*, 284.8789); this was followed by 3-*bromo*-4-*aza-azulene* (15 mg, 7%) as a green oil, *m/z* 206.9661 (M^+) (C_9H_6BrN requires *M*, 206.9684). Further elution gave 1-*bromo*-4-*aza-azulene* as a very unstable green oil (125 mg, 60%), *m/z* 206.9669 (M^+) (C_9H_6BrN requires *M*, 206.9684), and finally 4-aza-azulene (**1**) (16 mg) was recovered. For spectroscopic data, see Table 3.

In a similar experiment, treatment of compound (**1**) (0.17 g, 1.3 mmol) in CH_2Cl_2 (50 ml) and acetic acid (50 ml) with NBS (0.6 g, 3.3 mmol) gave, after chromatography, 1,3-dibromo-4-aza-azulene (243 mg, 68%).

Reaction of 4-Aza-azulene (**1**) *with Trifluoroacetic Anhydride* (*TFAA*).—To a stirred solution of compound (**1**) (19 mg, 0.14 mmol) in CH_2Cl_2 (5 ml) was added dropwise TFAA (0.5 ml, 1.58 mmol). The solution was stirred at room temperature for 30 min. T.l.c. indicated that compound (**1**) had been consumed to give blue base-line material. After concentration the solution was chromatographed using $CHCl_3$ as eluant. The original blue band (R_F 0) gradually disappeared with the appearance of a blue band further down the column. This was identified as starting material.

In an attempt to isolate the expected salt, *N*-trifluoroacetyl-4-aza-azulenium trifluoroacetate, removal of the solvent from a similar reaction mixture gave only tarry material.

Table 6. ^{13}C N.m.r. data for dimer (**14**)

Carbon	δ_C (p.p.m.)	Carbon	δ_C (p.p.m.)	$^1J_{CH}$ (Hz)
C=O	166.4	C=*C*H	137.7	175.1
	166.0		135.8	162.8
	165.3		131.9	161.8
	164.2		130.3	174.3
	163.4		130.2	174.3
	163.3		128.3	172.0
	162.8		126.9	171.7
C=C	144.9		125.4	159.3
	139.1		123.3	158.4
	137.0		108.2	159.5
	136.2		105.2	157.6
	132.9	CH	56.5	149.1
	128.1		55.6	145.0
	125.7		53.1	120.5
	117.8			
	111.3			
C(quaternary)	82.7			
	80.4			
	74.7			
CH_3	56.5			
	55.6			
	53.6			
	53.4			
	53.1			
	52.4			
	52.1			
	51.9			

Reaction of 4-Aza-azulene (**1**) *with MCPBA.*—MCPBA (0.169 g, 0.98 mmol) was added to a solution of compound (**1**) (0.085 g, 0.66 mmol) in CH_2Cl_2 (50 ml) and the resulting solution was stirred for 2 h at room temperature. The blue solution was concentrated and chromatographed directly using chloroform as eluant to give 4-*aza-azulene*-N-*oxide* (**22**) as a moderately stable green crystalline solid (76 mg, 79%), *m/z* 145.0528 (M^+) (C_9H_7NO requires *M*, 145.0528).

Reactions of 4-Aza-azulene (**1**) *with DMAD.*—A solution of compound (**1**) (0.28 g, 2.17 mmol) in CH_2Cl_2 (10 ml) was treated with DMAD (2 ml, 16.3 mmol). The mixture was stirred at room temperature in the dark for 9 days, and then chromatographed directly using chloroform as eluant to give a brown oil (0.79 g). This was purified by medium-pressure chromatography to give a small amount of starting material (0.03 g) followed by an unstable purple oil (0.17 g). Mass spectrometry gave a peak at *m/z* 459 which is thought to be a fragment ion. We were unable to identify this product conclusively.

Using the same solvent the adduct (**15**) as a yellow oil (0.23 g) was then eluted from the column, *m/z* 555 (M^+) 524, 496, 464, 432, 421, 346, and 258. The ^{1}H n.m.r. data are recorded in Table 4 together with decoupling information. ^{13}C N.m.r. data are collected in Table 5.

Finally, the dimeric adduct (**14**) was eluted as a red oil (0.30 g) which crystallised as red plates, m.p. 195—196 °C (from ethyl acetate–light petroleum); *m/z* 413 (M^+) 381, 354, and 322. Its n.m.r. data are given in Tables 6 and 7.

The total yield of products (based on starting material consumed) was 53%.

In a similar reaction 4-aza-azulene (**1**) (0.28 g) was dissolved in acetonitrile (10 ml) and treated with DMAD (2 ml) at room temperature in the dark. After 24 h the reaction was complete (no starting material remaining). After work-up as before, the three adducts were obtained in the same order in yields of 53, 142, and 77 mg, respectively.

Table 7. ^{1}H N.m.r. data for dimer (**14**)

H	δ_H (multiplicity)	$J_{H,H}$ (Hz)
1	5.86 (d)	10.2
2	4.88 (dd)	10.2, 7.0
3	5.67 (d)	10.9
4	6.12 (d)	10.9
5	5.68 (dd)	5.8, 1.6
6	5.82 (dd)	5.8, 2.6
7	3.07 (br t)	4.3, 2.6, 1.6
8	3.20 (dd)	7.2, 4.3
9	4.43 (dd)	7.2, 2.3
10	5.51 (br s)	
11	6.22 (d)	11.0
12	5.63 (dd)	11.0, 6.3
13	4.97 (dd)	10.2, 6.3
14	6.10 (d)	10.2

Reaction of 4-*Aza-azulene* (**1**) *with DEAD.*—Compound (**1**) (0.28 g, 2.17 mmol) in CH_2Cl_2 (10 ml) was treated with an excess of DEAD (2.5 ml) at room temperature during 6 days. Chromatography [$CHCl_3$–light petroleum (1:1)] gave, firstly, unchanged DEAD, followed by a blue fraction (0.39 g). This blue fraction, when subjected to further purification by medium-pressure chromatography (ether as eluant), gave firstly *N,N'*-bis(ethoxycarbonyl)-*N*-(4-aza-azulen-1-yl)hydrazine (**19**) (150 mg, 23%) as a blue oil, δ_H (500 MHz; $CDCl_3$) 1.20 (6 H, t, CH_3), 4.20 (4 H, q, CH_2), 7.21 (1 H, t, *J* 4.4 Hz, 7-H), 7.30 (1 H, t, *J* 6.7 Hz, 6-H), 7.47 (1 H, d, *J* 2.3 Hz, 3-H), 8.00 (1 H, br s, 8-H), 8.24 (1 H, d, 2-H), 8.43 (1 H, d, *J* 6.7, 5-H), and 9.30 (1 H, br s, NH); δ_C (125 MHz; $CDCl_3$) 14.5 and 15.3 (CH_3), 61.9 and 62.0 (CH_2), 127.9 (C-1), 141.6 (C-2), 117 (C-3), 156.0 (C-3a), 141.0 (C-5), 130.1 (C-6), 126.9 (C-7), 133.8 (C-8), 127.5 (C-8a), and 154.6 and 156.5 p.p.m. (CO); *m/z* 303 (M^+, 77%), 277 (5), 259 (3), 230 (94), 216 (16), and 184 (34).

Further elution gave *NN'*-bis(ethoxycarbonyl)-*N*-(4-aza-azulen-3-yl)hydrazine (**20**) (47 mg, 7%) as a blue oil, δ_H 1.20 (6 H, dt, CH_3), 4.15 (4 H, dq, CH_2), 7.24 (2 H, m, 1- and 7-H), 7.29 (1 H, d, *J* 4.5 Hz, 2-H), 7.32 (1 H, dd, *J* 10.5 and 6.4 Hz, 6-H), 8.15 (1 H, d, *J* 8.5 Hz, 8-H), 8.38 (1 H, d, *J* 6.4 Hz, 5-H), and 9.00 (1 H, br s, NH); δ_C 14.41 and 14.46 (CH_3), 61.9 and 62.9 (CH_2), 113.7 (C-1), 104.2 (C-2), 129.6 (C-3), 145.0 (C-3a), 141.2 (C-5), 130.4 (C-6), 127.9 (C-7), 136.7 (C-8), 134.5 (C-8a), and 155.8 and 156.1 p.p.m. (CO); *m/z* 303 (M^+, 11%), 277 (5), 259 (4), 239 (13), 230 (10), 216 (8), and 185 (27).

Finally, diethyl hydrazine-1,2-dicarboxylate (10 mg) was obtained as a white crystalline solid, m.p. 131—133 °C (lit.,[26] 133—134 °C).

X-*Ray Crystallographic Data for the Dimer* (**14**).—Crystals of the dimer (**14**) are monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 18.288(5)$, $b = 12.498(4)$, $c = 17.237(5)$ Å, $\beta = 97.81(1)°$, $D_c = 1.41$ g cm^{-3}, and μ(Cu-K_α) = 8.25 cm^{-1}. A total of 6 133 reflections was measured in the ω–2θ mode with $3 \leqslant \theta \leqslant 29$ on a Philips PW1100 four-circle diffractometer, of which 1 606 were regarded as unobserved [$I < 2\sigma(I)$]. The reflections, scanned over 0.8° (θ) at a speed of 0.032° (θ) s^{-1}, were corrected for background and Lorentz polarisation effects only. The structure was solved by direct methods and refined by blocked-matrix least-squares techniques using the program SHELX.[27] All the non-hydrogen atoms were refined anisotropically, and the positions of all the hydrogen atoms were obtained from difference Fourier synthesis. Convergence, using all data and σF^{-2} weights and a common isotropic thermal parameter for the hydrogen atoms (0.085 Å^2), was reached at $R_w = \Sigma w|\Delta F|/\Sigma w|F_o| = 4.9\%$ and $R = \Sigma|\Delta F|/\Sigma|F_o| = 6.8\%$. The maximum noise level of the final difference electron density map was 0.3 e Å^{-3}. Table 8 gives the fractional atom co-ordinates of the non-hydrogen atoms for compound (**14**).*

Table 8. Fractional atomic co-ordinates ($\times 10^4$) for the dimer (**14**)

	x	*y*	*z*
C(1)	3 061(1)	4 040(2)	3 516(1)
C(2)	2 354(2)	4 362(2)	3 487(2)
C(3)	1 865(2)	3 781(2)	3 947(2)
C(4)	2 160(1)	3 179(2)	4 557(2)
N(4A)	2 935(1)	3 070(2)	4 699(1)
C(5)	3 296(2)	3 415(2)	5 424(2)
C(6)	3 997(2)	3 665(3)	5 654(2)
C(7)	4 623(2)	3 676(2)	5 235(2)
C(8)	4 671(2)	3 235(2)	4 540(2)
C(8A)	4 069(1)	2 597(2)	4 080(2)
C(8B)	3 941(1)	1 458(2)	4 452(2)
C(9)	4 439(2)	580(2)	4 268(2)
C(9A)	4 088(2)	−247(2)	3 897(2)
C(10)	4 421(2)	−1 262(3)	3 700(2)
C(11)	4 314(2)	−1 682(3)	2 988(2)
C(12)	3 886(2)	−1 180(3)	2 324(2)
C(13)	3 309(2)	−529(3)	2 296(2)
N(13A)	2 934(1)	−181(2)	2 915(1)
C(14)	2 187(2)	8(2)	2 777(2)
C(15)	1 766(1)	−120(2)	3 361(2)
C(16)	2 079(1)	−779(2)	4 026(2)
C(17)	2 814(1)	−857(2)	4 190(1)
C(17A)	3 260(1)	−62(2)	3 764(1)
C(17B)	3 167(1)	1 103(2)	4 050(1)
C(18)	2 960(1)	2 027(2)	3 458(1)
C(18A)	3 264(1)	3 014(2)	3 968(1)
C(19)	3 504(2)	2 050(2)	2 867(2)
C(20)	4 145(2)	2 377(2)	3 231(2)
C(21)	3 600(2)	4 600(2)	3 077(2)
O(22)	4 169(1)	4 978(2)	3 368(1)
O(23)	3 356(1)	4 612(2)	2 313(1)
C(24)	3 826(2)	5 134(4)	1 821(1)
C(25)	2 030(2)	5 246(3)	2 968(2)
O(26)	1 457(1)	5 166(2)	2 549(1)
O(27)	2 450(1)	6 109(2)	3 019(1)
C(28)	2 187(2)	6 975(3)	2 495(2)
C(29)	1 044(2)	3 904(3)	3 724(2)
O(30)	697(1)	4 628(2)	3 942(1)
O(31)	788(1)	3 136(2)	3 230(1)
C(32)	−29(2)	3 183(3)	2 989(2)
C(33)	1 694(2)	2 567(3)	5 055(2)
O(34)	1 038(1)	2 670(2)	5 006(1)
O(35)	2 096(1)	1 877(2)	5 518(1)
C(36)	1 709(2)	1 261(3)	6 047(2)
C(37)	1 875(2)	350(3)	1 956(2)
O(38)	2 006(1)	1 194(2)	1 683(1)
O(39)	1 481(1)	−428(2)	1 593(1)
C(40)	1 112(2)	−172(4)	807(2)
C(41)	1 016(2)	334(3)	3 266(2)
O(42)	719(2)	762(2)	2 689(1)
O(43)	711(1)	240(2)	3 935(1)
C(44)	−26(2)	670(4)	3 924(2)
C(45)	1 574(2)	−1 457(3)	4 437(2)
O(46)	1 590(1)	−1 497(2)	5 136(1)
O(47)	1 117(1)	−2 007(2)	3 923(1)
C(48)	573(2)	−2 662(4)	4 218(3)
C(49)	3 176(2)	−1 673(3)	4 735(2)
O(50)	3 685(1)	−1 516(2)	5 245(1)
O(51)	2 864(1)	−2 626(2)	4 582(1)
C(52)	3 129(2)	−3 514(3)	5 084(3)

* Tables of hydrogen-atom co-ordinates, temperature factors, and bond lengths and angles are given in Supplementary Publication No. SUP 56262 (15 pp.). For details of the Supplementary Publications Scheme, see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1. Structure factors are available from the editorial office on request.

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References

1 Preliminary communication, O. Meth-Cohn and C. Moore, *J. Chem. Soc., Chem. Commun.*, 1983, 1246.
2 For a recent review, see T. Nishiwaki and N. Abe, *Heterocycles*, 1981, **15**, 547.
3 T. Nozoe, S. Seto, S. Matsumura, and T. Terasawa, *Chem. Ind. (London)*, 1954, 1357.
4 K. Hafner and M. Kreuder, *Angew. Chem.*, 1961, **73**, 657.
5 K. Hafner, *Chimia*, 1973, **27**, 640; *Lect. Heterocycl. Chem.*, 1976, **3**, 33 (*Chem. Abstr.*, 1976, **85**, 123677p). No full experimental details or properties of 6-aza-azulene appear to have been published.
6 M. K. Conner and E. LeGoff, *Tetrahedron Lett.*, 1970, 2687.
7 W. Lwowski, 'Nitrenes,' Interscience. New York, 1970.
8 M. Clancy, D. G. Hawkins, M. M. Hesabi, O. Meth-Cohn, and S. Rhouati, *J. Chem. Res. (S)*, 1982, 78.
9 O. Meth-Cohn and S. Rhouati, *J. Chem. Soc., Chem. Commun.*, 1980, 1161; 1981, 241; O. Meth-Cohn, D. Patel, and S. Rhouati, *Tetrahedron Lett.*, 1982, **23**, 5085; D. G. Hawkins, O. Meth-Cohn, and S. Rhouati, *J. Chem. Soc., Chem. Commun.*, 1983, 1254.
10 'Rodd's Chemistry of Carbon Compounds,' 2nd edn., Elsevier, New York, 1977, vol. IIIG, p. 293.
11 A. G. Anderson, R. Scotini, E. J. Cowles, and C. G. Fritz, *J. Org. Chem.*, 1957, **22**, 1193.
12 R. M. Acheson and N. F. Elmore, *Adv. Heterocycl. Chem.*, 1978, **23**, 263.
13 (*a*) N. Abe, Y. Tanaka, and T. Nishiwaki, *J. Chem. Soc., Perkin Trans. 1*, 1978, 492; (*b*) K. Hafner and J. Häring, *Erdoel Kohle, Erdgas, Petrochem.*, 1979, **32**, 136; (*c*) K. Hafner, J. Häring, and W. Jakel, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 159.
14 D. Cremer and J. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1358.
15 C. Altona and M. Sundaralingham, *J. Am. Chem. Soc.*, 1972, **94**, 8205; J. C. A. Boeyens, *J. Cryst. Mol. Struct.*, 1978, **8**, 317; I. Boessenkool and J. C. A. Boeyens, *ibid.*, 1980, **10**, 11.
16 R. K. Smalley, 'Comprehensive Heterocyclic Chemistry,' Penguin, 1984, vol 7, p. 520.
17 W. Flitsch and U. Krämer, *Adv. Heterocycl. Chem.*, 1978, **22**, 321.
18 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1984, 175, and personal communication.
19 R. Weissgerber, *Ber. Deutsch. Chem. Ges.*, 1911, **44**, 1436.
20 C. M. Suter and G. A. Lutz, *J. Am. Chem. Soc.*, 1938, **60**, 1360.
21 C. M. Suter and H. B. Milne, *J. Am. Chem. Soc.*, 1940, **62**, 3473.
22 J. P. Quere and E. Maréchal, *Bull. Soc. Chim. Fr.*, 1971, **8**, 2983.
23 D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Am. Chem. Soc.*, 1968, **90**, 5498.
24 H. O. House and C. B. Hudson, *J. Org. Chem.*, 1970, **35**, 647.
25 L. C. King and G. K. Ostrum, *J. Org. Chem.*, 1964, **29**, 3459.
26 J. C. Kauer, *Org. Synth.*, Coll. Vol. IV, 1963, p. 411.
27 G. M. Sheldrick, 'SHELX. A Program for Crystal Structure Determination,' University of Cambridge, 1976.

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