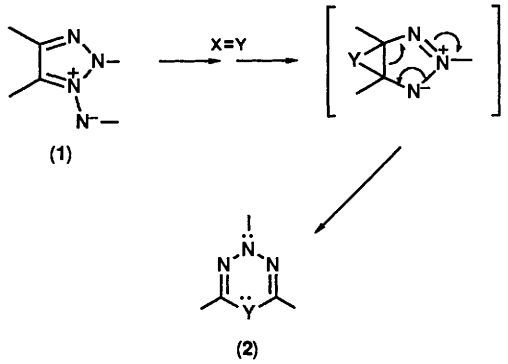
8π-Six-Atom Rings: 1,3,4,5-Oxa- and -Thia-triazines and 1,2,3,5-Tetrazines from an Extended Tandem Reaction: Reactions of 1,2,3-Triazolium-1-imides with (*E*)-Cinnamaldehyde, Methyl Cyanodithioformate, and Aryl-*N*-sulphinylamines: New Tetrahydro-oxazolo[4,5-*d*]-1,2,3-Triazoliumides and Triazaspiro-[4.4]nonanes. Azolium 1,3-Dipoles. Part 4.†

Richard N. Butler,* Ann M. Evans, Eithne M. McNeela, Gerard A. O'Halloran, Paul D. O'Shea, Desmond Cunningham, and Patrick McArdle
Chemistry Department, University College, Galway, Ireland

The reactions of substituted 1,2,3-triazolium-1-imides with (*E*)-cinnamaldehyde, methyl cyanodithioformate, and aryl-*N*-sulphinylamines gave rise to substituted 1,3,4,5-oxatrizines, 1,3,4,5-thiatriazines, and 1,2,3,5-tetrazines, respectively. Each of these is an 8π-six-atom ring. The routes were similar in each case and involved an extended tandem sequence of cycloaddition, rearrangement, fragmentation, and ring expansion. New oxazolo[4,5-*d*]-1,2,3-triazoles which were formed along the route to the 1,3,4,5-oxatriazines were isolated as stable compounds. The structures and reactivity of the 8π-six-atom rings are discussed. X-Ray crystal structures are reported for 4-(*p*-bromophenyl)-2,6-diphenyl-4*H*-1,3,4,5-oxatriazine (**6b**); 2,4,6-triphenyl-4*H*-1,3,4,5-thiatriazine (**11a**); 5-(*p*-bromophenyl)-2,5-dihydro-2,4,6-triphenyl-1,2,3,5-tetrazine (**17b**); 2,6-bis(*p*-bromophenyl)-3a,5,6,6a-tetrahydro-3a,6a-diphenyl-5*exo*-styryloxazolo[4,5-d]-1,2,3-triazol-2-ium-1-ide (**4b**); and 4-[(5′-methylisoxazol-3′-yl)imino]-2-(*p*-nitrophenyl)-1,2,3-triazaspiro-[4.4]non-1-en-2-ium-3-ide (**19b**).

The monocyclic high-nitrogen azines (containing three linked N atoms) represent classes of compounds which are little known[1]. There are but few routes to the monocyclic 1,2,3-triazine structure (**2**) and in the tetrazine series the monocyclic 1,2,3,5-tetrazine ring is by far the least studied.[2–4] Herein we report a new convenient route to high yields of the oxygen, nitrogen, and sulphur derivatives of structure (**2**) (Scheme 1). In Part 3 of the series[5] we have described a new general reaction of 1,2,3-triazolium-1-imide 1,3-dipoles (**1**) which involves a tandem cycloaddition and sigmatropic rearrangement. When this reaction was applied to dipolarophiles of type >C=O, >C=S, and –N=S=O the tandem sequence built up into an extended run of reactions. These opened up a novel ring-expansion methodology (Scheme 1) for entry to the new and rare 8π-six-atom heterocycles (**2**) from the 1,2,3-triazolium imide substrates. Syntheses and detailed structures of the 8π-six-atom rings (**2**) are described.[6]



Scheme 1.

Results and Discussion

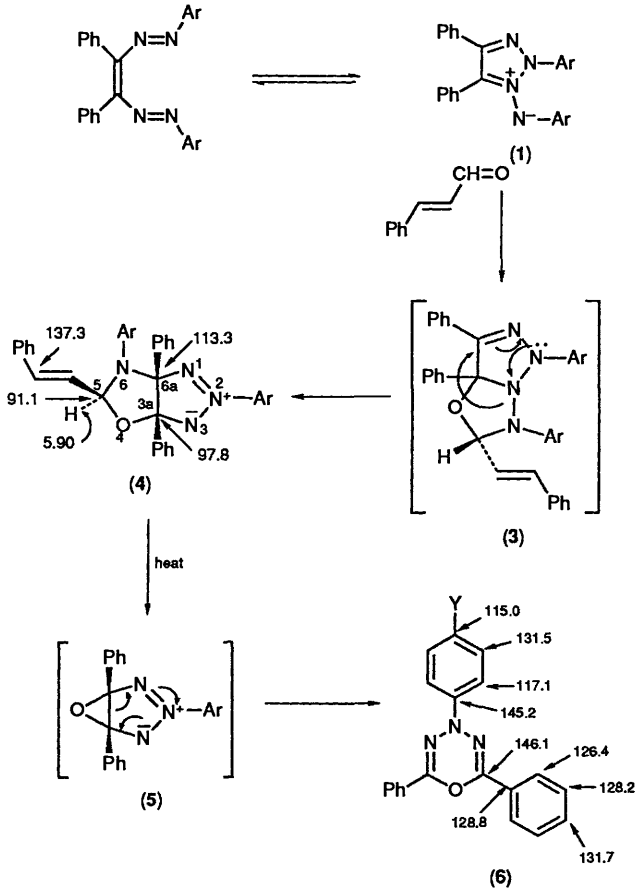
(*i*) 1,3,4,5-*Oxatriazines and* 3a,5,6,6a-*Tetrahydro-oxazolo* [4,5-d]-1,2,3-*triazoles*.—Triazolium imide 1,3-dipoles when heated in ethyl methyl ketone with (*E*)-cinnamaldehyde reacted at the carbonyl group to give a new ring system, the tetrahydro-oxazolo [4,5-*d*]-1,2,3-triazoles (**4**) (Table 1). This was the only case where the dipole reacted with a carbonyl group. Such reactions were not observed with benzaldehydes or with aliphatic ketones such as ethyl methyl ketone which could be used as a solvent. The reaction which proceeded through the sequence shown in Scheme 2 is another example of the tandem 1,3-dipolar cycloaddition and sigmatropic rearrangement described in Part 3 where its kinetics have been reported.[5] The X-ray crystal structure of compound (**4b**) is shown in Figure 1. In accordance with the mechanism established[5] for this reaction the styryl substituent in compounds (**4**) is in the *exo*-position. The products (**4**) were stable under ambient conditions. However, on being heated under reflux in ethanol for 30 min or in ethanol containing acetic acid (10 min) they changed into red 1,3,4,5-oxatriazines (**6**) probably *via* the corresponding intermediate (**5**). There is only one previous report[7] of this 8π-six-atom ring system. It was obtained from photolysis of relatively inaccessible 1,2,3-triazole-1-oxides. We confirmed this photolytic route for compound (**6a**) but we found it to be more tedious and to give a lower yield than the present route (Table 1). An X-ray crystal structure was reported[7] but an apparently flat ring structure was presented as 'an average structure' taking into account stacking effects in the crystals. Good crystals of these

† Part 3 is ref. 5.

Table 1. 8π-Six-atom rings and other products.

Entry	Substituents R,R,	Ar	Ar′	Product Compd.	M.p. (°C)	Yield (%)	Microanalysis Found % (Required %) C	H	N
1	Ph,Ph	Ph		**(6a)**	171[b]	90	76.5(76.7)	5.0(4.8)	13.4(13.4)
2	Ph,Ph	*p*-BrC_6H_4		**(6b)**	179[b]	81	61.3(61.2)	3.7(3.6)	10.7(10.7)
3	Ph,Ph	Ph		**(4a)**	178[c,g]	80	80.6(80.7)	5.6(5.4)	10.75(10.75)
4	Ph,Ph	*p*-BrC_6H_4		**(4b)**	183[d]	82	62.4(62.9)	3.9(3.8)	8.1(8.3)
5	Ph,Ph	Ph		**(11a)**	113[e]	84	72.7(72.9)	4.7(4.5)	12.5(12.7)
6	Ph,Ph	*p*-BrC_6H_4		**(11b)**	146[b]	91	58.9(58.8)	3.3(3.4)	10.2(10.3)
7	Ph,Ph	*p*-$NO_2C_6H_4$		**(11c)**	193[f]	86	63.8(64.1)	3.9(3.7)	14.8(14.9)
8	Ph,Ph	Ph	Ph	**(17a)**	197[f]	83	80.7(80.4)	5.5(5.2)	14.3(14.4)
9	Ph,Ph	Ph	*p*-BrC_6H_4	**(17b)**	207[f]	71[i]	67.0(66.8)	4.2(4.1)	12.0(12.0)
10	Ph,Ph	Ph	*p*-$NO_2C_6H_4$	**(17c)**	246[f]	78[i]	72.2(72.0)	4.6(4.4)	15.9(16.1)
11	Ph,Ph	Ph	5-Meoxaz[a]	**(17d)**	192[b]	75[i]	73.2(73.3)	4.8(4.9)	17.6(17.8)
12	Ph,Ph	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	**(17e)**	236[f]	83	65.0(65.2)	3.9(4.0)	17.3(17.6)
13	Ph,Ph	*p*-$NO_2C_6H_4$	5-Meoxaz[a]	**(17f)**	218[f]	75[j]	65.9(65.7)	4.3(4.1)	19.0(19.2)
14	$[CH_2]_5$	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	**(17g)**	217[f]	84	57.6(57.9)	4.8(4.6)	21.6(21.3)
15	$[CH_2]_4$	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	**(19a)**	209[f]	47	56.6(56.8)	4.3(4.2)	22.0(22.1)
16	$[CH_2]_4$	*p*-$NO_2C_6H_4$	5-Meoxaz[a]	**(19b)**	182[g]	10	56.4(56.5)	4.9(4.7)	24.4(24.7)
17	Ph,Ph	Ph	*p*-BrC_6H_4	**(15)**	182[h]	10[k]	63.7(63.4)	4.2(4.0)	11.3(11.6)

[a] 5-Methylisoxazol-3-yl. [b] From EtOH. [c] From Et_2O. [d] From MeCOEt. [e] From MeOH. [f] From Pr^nOH. [g] From hexane. [h] Purified by careful recrystallization from EtOH (labile, may fragment during attempted purification). [i] **(17a)** (10–12%) was also isolated. [j] **(17e)** (18.5%) was also isolated. [k] Isolated along with **(17b)** (71%) and **(17a)** (10%).



Scheme 2. Ar = (*a*), Ph; (*b*), *p*-BrC_6H_4. Some ^1H and ^{13}C NMR shifts are shown for *p*-Br derivatives.

compounds were not easy to obtain but eventually good crystals were grown in slowly evaporating ethereal solutions and the clear X-ray structure of compound **(6b)**, Figure 2, was obtained. The ring adopts a boat shape with equatorial substituents, thus eliminating any question[7] of a 6π-aromatic structure being favoured through extensive electronic delocalization or reorganization. This ring shows the same structure as the sulphur and nitrogen analogues (below) and this boat shape is the normal structure of 8π-six-atom rings. These results and others[8] suggest that 8π-six-atom rings of high nitrogen:carbon heterocycles require a boat structure for stability.

The oxatriazines **(6)** were remarkably stable to acids (CF_3CO_2H,AcOH) and oxidizing agents (Pb^{IV}) and they did not react with 4π-systems such as 2,3-dimethylbutadiene or the highly reactive 1,3-dipole benzonitrile *N*-*p*-nitrophenylimide (a nitrilimine). They were susceptible to nucleophilic attack at C-2 by aniline (giving benzanilide) and by sodium hydroxide (giving sodium benzoate). The only other products isolated from these nucleophilic reactions were gums.

(*ii*) 1,3,4,5-*Thiatriazines*.—A sulphur atom was introduced into the structure **(2)** when methyl cyanodithioformate **(7)** was used as dipolarophile to the triazolium imide 1,3-dipole **(1)** (Scheme 3). Thus treatment of the dipoles **(1)** with compound **(7)** for short periods in benzene at ambient temperatures gave high yields of the products **(11)** (Table 1). These are the first examples[6] of the parent 1,3,4,5-thiatriazine ring structure. There is only one previous report[9] of this ring system. The oxidized form corresponding to **(2**; Y = SO_2) was obtained in low yield among the products of the reaction of substituted thiirene 1,1-dioxides with azide ion.[9] The oxidized form of the ring was labile to loss of SO_2 and the reduced parent ring was hitherto unknown. By analogy with the reactions already described we suggest that compounds **(11)** are formed by an extended tandem reaction, running through at least four transition states as the starting materials give rise to stable products (Scheme 3). The product **(9)** [analogous to **(4)**] in this case was not stable and none of the intermediates along the sequence could be detected owing to the rapidity of the reactions. The fragment eliminated in the step **(9)** ⟶ **(10)** was detected only as a small quantity of resin. This resin may have been derived from an imine

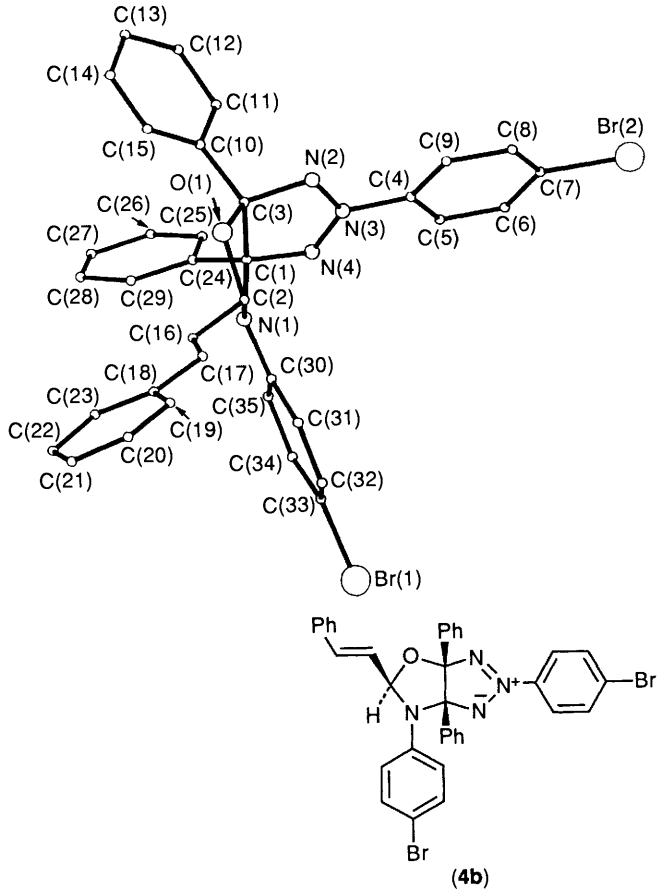


Figure 1. X-Ray molecular structure of compound (**4b**).

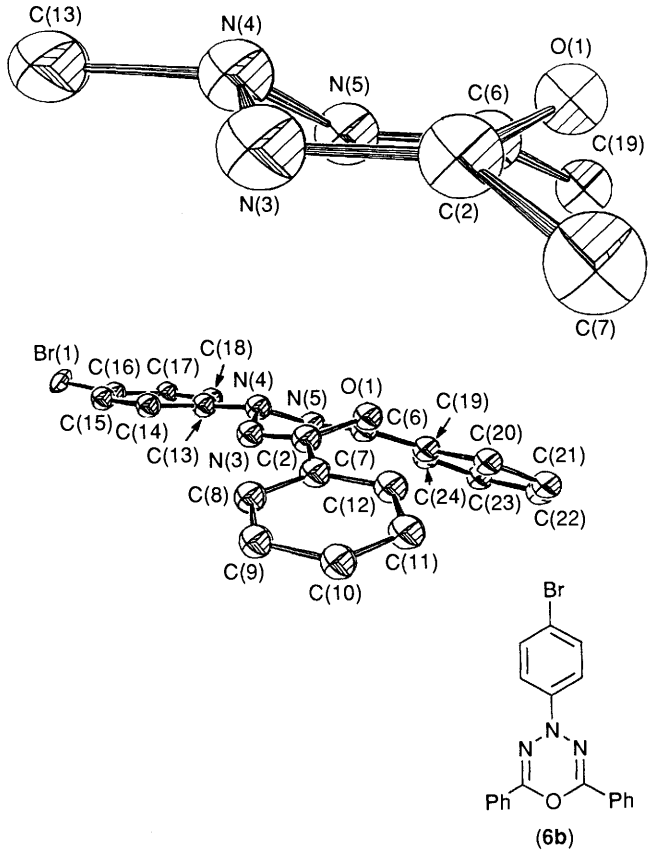


Figure 2. X-Ray molecular structure of compound (**6b**) with (top) detail of the 8π-oxatriazine ring. The molecule lies on a crystallographic mirror plane. The unlabelled atoms are generated by operation of the mirror plane.

[MeS(CN)C=NAr] since no methanethiol was generated during the reaction.

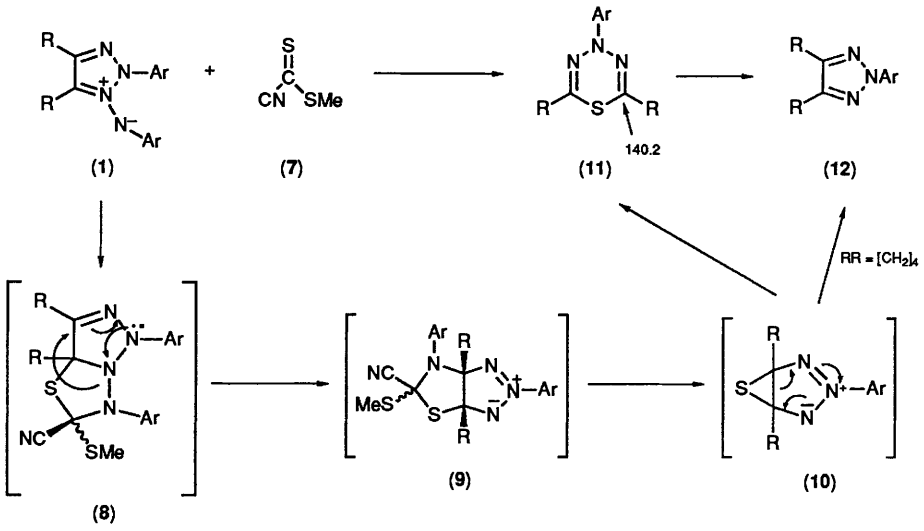
The most notable feature of the 1,3,4,5-thiatriazine ring was a ready desulphurization with ring contraction to the known 1,2,3-triazoles (**12**). When chromatography of the compounds (**11**) was attempted on an alumina column with chloroform the triazoles (**12**) were obtained in quantitative yield. Attempted oxidation to the sulphone derivative with *m*-chloroperbenzoic acid (MCPBA) also gave the triazole in quantitative yield. This easy loss of sulphur from the non-aromatic ring (**11**) to give the aromatic triazole (**12**) is related to the more common chelotropic[10] expulsions of SO_2 from cyclic sulpholenes to give polyenes.[11,12] The substrates (**11**) are 8π-systems and the reaction should be a linear, conrotatory[10] expulsion of sulphur, rotating the *C*-aryl rings up into the plane of the new triazole ring (see Figure 3). The X-ray crystal structure of compound (**11a**) is shown in Figure 3. It is a boat structure similar to that of compound (**6b**). In both cases the 8π-six-atom ring is avoiding a potentially antiaromatic planar structure and the substituents are equatorial, thus ensuring that adjacent lone-pairs are at angles close to 90° (thereby conforming with the '*gauche* effect'*). The boat structure with the S atom above the plane of the two C=N moieties as well as the axial aryl substituents is structurally favourable for an aromatization by an easy linear expulsion of sulphur away from the ring, with concerted conrotatory upward motion of both *C*-aryl groups.

(*iii*) 1,2,3,5-*Tetrazines and* 1,2,3-*Triazaspiro*[4.4]*nonanes*.—The extended tandem reaction of Schemes 2 and 3 consists of a 1,3-dipolar cycloaddition, sigmatropic rearrangement, ring fragmentation, and sigmatropic ring expansion. A similar reaction was achieved as a new route to 1,2,3,5-tetrazines (**17**) using *N*-sulphinylamines (**13**)† as dipolarophiles. In this case it proved possible to find further experimental support for the overall tandem reaction sequence. When the substituted 1,2,3-triazolium imides (**1**) were heated with aryl-*N*-sulphinylamines (**13**) in benzene the new 1,2,3,5-tetrazines (**17**) were obtained in high yield (Table 1). We envisage their formation *via* the steps (**14**) ⟶ (**15**) ⟶ (**16**) ⟶ (**17**) (Scheme 4), in another example illustrating the generality and scope of this tandem sequence. In the step (**15**) ⟶ (**16**) loss of a molecule of *N*-sulphinylamine from intermediate (**15**) may occur in either of two ways when the Ar and Ar′ substituents are different: both expected products (**17**) were obtained but in general the lower-molecular weight PhNSO was lost preferentially. In one case it proved possible to isolate compound (**15**; R = Ar = Ph; Ar′ = *p*-BrC_6H_4) in *ca.* 10% yield (Table 1). It was characterized by its ^{13}C NMR spectrum (which showed the characteristic bridgehead carbons) and microanalysis. It was unstable and on attempted recrystallization or simply warming in benzene it gave the expected mixture of products (**17**) in a ratio identical with that reached by the direct reaction of compound (**1**) with *p*-bromo-*N*-sulphinylaniline.

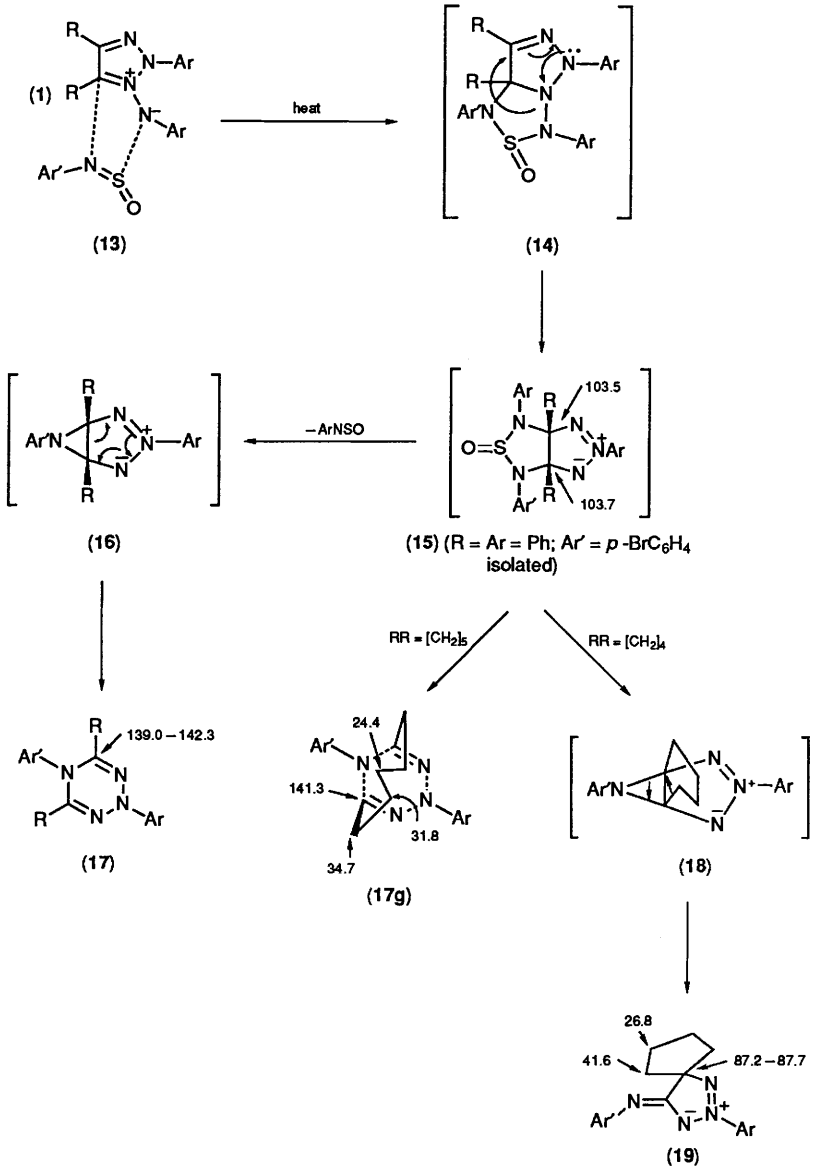
In the sequence of reactions in Schemes 2, 3, and 4 the 8π-ring

* The *gauche* effect is the preferred near-perpendicular arrangement of lone-pairs in heterocycles containing heteroatom–heteroatom bonds.

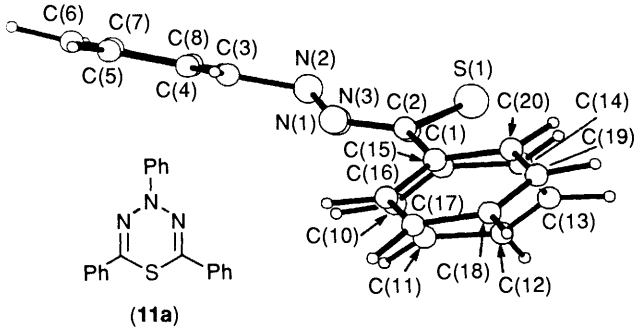
† *N*-Sulphinylamines are unstable, moisture-sensitive compounds. An X-ray structure of one has recently shown them to have the *cis*-structure (**13**) with expanded valency on sulphur.[14]



Scheme 3. ^{13}C NMR shifts in $CDCl_3$ are shown.

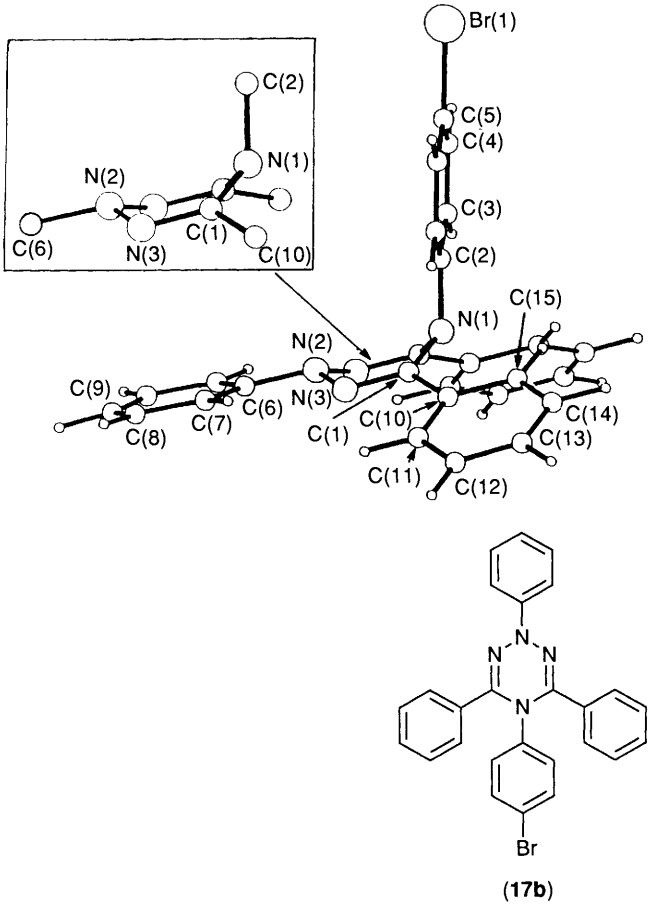


Scheme 4. Some ^{13}C NMR shifts in $CDCl_3$ are shown. For (**1**), Ar = (*a*) Ph; (*b*), *p*–BrC_6H_4; (*c*), *p*–$NO_2C_6H_4$; for Ar′ see Table 1.



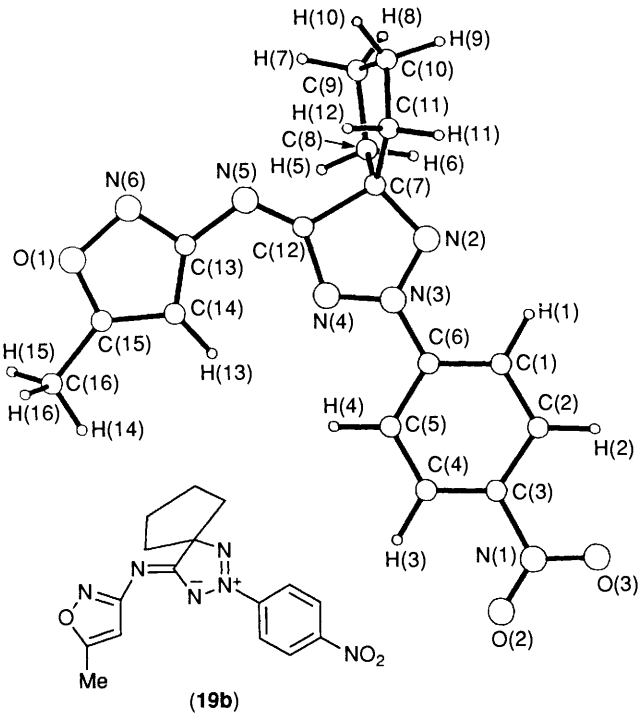
(11a)

Figure 3. X-Ray molecular structure of compound (**11a**).



(17b)

Figure 4. X-Ray molecular structure of compound (**17b**) with (inset) detail of the 8π-1,2,3,5-tetrazine ring. The molecule lies on a crystallographic mirror plane. The unlabelled atoms are generated by operation of the mirror plane.



(19b)

Figure 5. X-Ray molecular structure of compound (**19b**).

is directly preceded by the proposed strained intermediates (**5**), (**10**), and (**16**). Ring expansion in these by a preferred disrotatory outward electrocyclic process relieves strain at the tetrahedral bridgehead carbons, thereby forming the 8π-rings. In theory this disrotatory outward process could be sterically constricted by linking the two bridgehead R substituents. When RR = $[CH_2]_5$ the ring expansion still occurred, giving compound (**17g**) (Scheme 4, Table 1) but when the bridgehead link-chain was shortened to four carbons, RR = $[CH_2]_4$, the disrotatory outward process was indeed prevented. The intermediate (**18**) reacted instead by opening of the strained aziridine moiety with a 1,2-shift involving ring contraction of the fused cyclohexane ring to a spiro cyclopentane, giving the new fused products (**19**) (Table 1). This observation supports the presence of the strained fused aziridine intermediate (**18**). Similar ring opening and 1,2-shifts have been reported[15] on thermal cleavage of crowded 1,2-dihalogenoaziridines. Accurate Dreiding models showed that the interesting structure (**17g**) was at the limit for bridging of the tetrazine carbons with a methylene chain and it was not possible to do so with a four-methylene-group bridge chain without breaking the tetrazine ring. When the bridgeheads were linked by four methylene groups in the reaction with compound (**7**) (Scheme 3) the product was the triazole (**12**; RR = $[CH_2]_4$) formed in 85% yield. It is likely that this triazole, formed in such a high yield at ambient temperatures, resulted from extrusion of sulphur from the intermediate (**10**) since deamination of the compounds (**1**) requires prolonged heating at temperatures > 100 °C.

X-Ray crystal structures of compounds (**17b**) and (**19b**) are shown in Figures 4 and 5, respectively (Scheme 4). The 1,2,3,5-tetrazine ring shows the expected boat structure with the N^5-substituent axial and the 4- and 6-aryl groups equatorial, conforming to the *gauche* effect.[13] The structures are further supported by the expected proton and carbon NMR signals.

(*iv*) *Structure of 8π-Six-atom Carbon–Nitrogen Heterocycles.*—The boat form for molecules with general structure (**2**) is preferred over a possible chair structure. Both halves of the molecule are planar and the bond lengths, particularly those of compounds (**11a**) and (**17b**), suggest conjugation in the N–N–C–Y units. Thus for compound (**17b**) the bond lengths N(1)–N(2), N(3)–C(4), and C(4)–N(5) were 1.39, 1.28, and 1.43 Å, respectively. These when compared with the values[16] for individual alternating single and double bonds N–N (1.41 Å), C=N (1.27 Å), and C–N (1.45 Å) suggest conjugation in the ring half-plane. Also, with compound (**11a**) the C–S bond length at 1.783 Å is longer than the normal C(sp^2)–S(divalent) distance[16] of 1.751 Å and shorter than the single C–S bond length[16] (1.82 ± 0.1 Å) of dimethyl sulphide, suggesting the presence of

Table 2. Fractional atomic co-ordinates for compound (**4b**).

Atom	*x*	*y*	*z*
Br(1)	0.356 34(15)	1.313 98(10)	−1.058 13(11)
Br(2)	0.320 7(2)	0.632 8(2)	−0.529 6(1)
C(10)	0.169 1(11)	0.601 2(8)	−1.185 1(8)
C(11)	0.060 2(12)	0.588 5(9)	−1.125 7(9)
C(12)	−0.023 2(14)	0.524 3(10)	−1.155 7(12)
C(13)	0.005 1(17)	0.473 3(11)	−1.246 4(12)
C(14)	0.117 5(17)	0.484 5(12)	−1.303 0(11)
C(15)	0.196 1(13)	0.547 7(9)	−1.271 6(9)
C(16)	0.485 7(13)	0.783 2(9)	−1.306 1(8)
C(17)	0.617 5(12)	0.750 2(9)	−1.323 5(9)
C(18)	0.684 5(15)	0.769 9(10)	−1.423 8(9)
C(19)	0.821 1(16)	0.722 3(12)	−1.433 2(11)
C(20)	0.890 9(18)	0.739 3(16)	−1.520 8(15)
C(21)	0.824 8(23)	0.805 0(17)	−1.599 2(13)
C(22)	0.688 4(25)	0.853 0(16)	−1.595 6(12)
C(23)	0.614 3(17)	0.834 9(14)	−1.506 2(12)
C(24)	0.066 1(11)	0.859 1(8)	−1.191 1(10)
C(25)	−0.061 1(15)	0.883 7(10)	−1.142 8(13)
C(26)	−0.177 8(17)	0.930 2(15)	−1.197 8(23)
C(27)	−0.174 5(30)	0.951 4(17)	−1.298 5(25)
C(28)	−0.052 9(24)	0.928 9(15)	−1.346 6(16)
C(29)	0.067 5(15)	0.882 2(11)	−1.294 5(12)
O(1)	0.371 4(7)	0.659 4(6)	−1.211 3(5)
N(1)	0.306 4(8)	0.849 9(6)	−1.176 3(5)
N(2)	0.301 8(8)	0.619 7(7)	−1.041 8(6)
N(3)	0.249 7(8)	0.707 0(7)	−0.984 6(6)
N(4)	0.180 4(8)	0.809 9(7)	−1.027 5(6)
C(1)	0.196 4(10)	0.802 6(8)	−1.136 1(7)
C(2)	0.426 8(10)	0.755 3(8)	−1.202 0(7)
C(3)	0.258 4(11)	0.667 0(8)	−1.144 7(7)
C(4)	0.267 9(10)	0.686 5(8)	−0.879 2(7)
C(5)	0.190 1(11)	0.772 7(10)	−0.819 0(8)
C(6)	0.208 4(12)	0.754 4(11)	−0.715 8(9)
C(7)	0.298 6(12)	0.652 5(10)	−0.672 1(8)
C(8)	0.372 5(12)	0.569 5(10)	−0.732 3(8)
C(9)	0.355 4(11)	0.586 2(9)	−0.836 0(8)
C(30)	0.321 2(10)	0.954 7(8)	−1.148 8(7)
C(31)	0.446 4(12)	0.975 1(9)	−1.143 4(8)
C(32)	0.456 3(12)	1.082 6(9)	−1.117 5(8)
C(33)	0.342 4(11)	1.169 0(9)	−1.096 8(7)
C(34)	0.217 1(11)	1.153 0(9)	−1.104 3(7)
C(35)	0.204 3(11)	1.046 0(8)	−1.128 0(7)

Table 3. Fractional atomic co-ordinates for a symmetrical half of compound (**6b**).

Atom	*x*	*y*	*z*
Br(1)	0.169 07(6)	0.250 00	−0.128 50(17)
O(1)	−0.168 5(4)	0.2500	0.975 3(12)
N(3)	−0.071 4(3)	0.179 9(4)	0.779 6(9)
N(4)	−0.064 5(5)	0.2500	0.656 6(12)
C(2)	−0.122 5(4)	0.182 6(4)	0.934 1(10)
C(7)	−0.138 0(4)	0.117 4(4)	1.093 2(10)
C(8)	−0.189 5(4)	0.129 6(4)	1.276 0(12)
C(9)	−0.198 1(5)	0.066 2(5)	1.429 6(14)
C(10)	−0.158 3(5)	−0.004 1(5)	1.402 2(13)
C(11)	−0.108 6(5)	−0.164 1(4)	1.219 2(13)
C(12)	−0.097 9(4)	0.045 9(4)	1.059 0(12)
C(13)	−0.005 6(5)	0.2500	0.485 9(16)
C(14)	0.021 3(4)	0.321 8(4)	0.397 5(10)
C(15)	0.075 9(4)	0.321 8(5)	0.216 6(12)
C(16)	0.100 1(6)	0.2500	1.131 6(15)

conjugation. Hence the molecules (**2**) contain two planar hydrazidine, hydrazide, or thiohydrazidine units with the end atoms shared. Models show that a chair structure would result

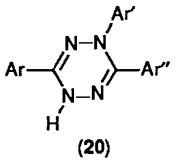
Table 4. Fractional atomic co-ordinates for compound (**11a**).

Atom	*x*	*y*	*z*
S(1)	0.015 11(16)	0.236 59(7)	0.033 01(11)
N(1)	0.137 9(5)	0.174 9(2)	−0.162 6(3)
N(2)	0.117 7(5)	0.113 2(2)	−0.094 7(3)
N(3)	0.179 4(4)	0.112 3(2)	0.028 9(3)
C(1)	0.142 4(5)	0.165 4(2)	0.093 6(4)
C(2)	0.099 4(6)	0.233 9(2)	−0.112 7(4)
C(3)	0.150 8(5)	0.049 0(2)	−0.159 3(4)
C(4)	0.185 5(6)	−0.013 1(3)	−0.096 0(4)
C(5)	0.212 7(6)	−0.075 2(3)	−0.159 4(5)
C(6)	0.202 5(7)	−0.075 0(3)	−0.286 3(5)
C(7)	0.165 8(7)	−0.013 0(3)	−0.350 2(5)
C(8)	0.139 9(6)	0.049 6(3)	−0.287 4(5)
C(9)	0.204 6(5)	0.168 0(2)	0.226 1(4)
C(10)	0.129 9(6)	0.211 6(3)	0.306 7(5)
C(11)	0.183 3(7)	0.209 8(3)	0.433 5(6)
C(12)	0.312 4(6)	0.165 6(3)	0.474 9(5)
C(13)	0.388 5(6)	0.123 1(3)	0.394 5(5)
C(14)	0.336 0(6)	0.124 1(3)	0.270 0(4)
C(15)	0.127 3(5)	0.301.8(2)	−0.177 6(4)
C(16)	0.221 8(5)	0.301 3(3)	−0.277 9(4)
C(17)	0.247 8(6)	0.364 5(3)	−0.340 1(5)
C(18)	0.175 7(7)	0.426 6(3)	−0.302 4(5)
C(19)	0.079 5(7)	0.427 4(3)	−0.205 7(5)
C(20)	0.054 2(6)	0.363 9(3)	−0.141 1(5)

Table 5. Fractional atomic co-ordinates for one of the symmetrical halves of compound (**17b**).

Atom	*x*	*y*	*z*
Br(1)	0.167 36(22)	0.250 00	0.106 59(18)
N(1)	0.439 8(12)	0.2500	−0.266 2(10)
N(2)	0.295 5(11)	0.2500	−0.407 3(10)
N(3)	0.355 0(8)	0.160 1(7)	−0.394 4(7)
C(1)	0.429 6(10)	0.162 1(9)	−0.325 6(8)
C(2)	0.372 7(14)	0.2500	−0.178 8(13)
C(3)	0.342 1(10)	0.160 4(10)	−0.135 7(8)
C(4)	0.279 8(11)	0.160 8(11)	−0.050 5(9)
C(5)	0.252 2(17)	0.2500	−0.009 8(14)
C(6)	0.208 3(16)	0.2500	−0.480 8(13)
C(7)	0.165 2(11)	−0.339 7(11)	−0.513 2(9)
C(8)	0.077 8(12)	0.338 5(11)	−0.582 4(9)
C(9)	0.036 8(17)	0.2500	−0.619 9(16)
C(10)	0.509 0(10)	0.078 2(9)	−0.311 7(8)
C(11)	0.502 5(11)	−0.005 3(10)	−0.369 2(9)
C(12)	0.577 3(11)	−0.086 5(11)	−0.356 4(9)
C(13)	0.656 5(12)	−0.082 6(11)	−0.283 6(8)
C(14)	0.663 0(13)	−0.001 9(10)	−0.225 3(9)
C(15)	0.591 2(11)	0.081 1(9)	−0.237 8(9)

in the loss of this planarity and also introduce a torsional twist into the C=N moieties in the ring. This boat shape is a primary structural constraint on 8π-six-atom carbon–nitrogen heterocycles. Recently in another context we have obtained[8] the X-ray crystal structure of a molecule in the series (**20**). This also adopted a boat structure, thereby constricting the annular tautomerism to suit the boat-shaped requirement. Controversial earlier oxidations of the structures (**21**) are now well known to



(**20**)

Table 6. Fractional atomic co-ordinates for compound (**19b**).

Atom	*x*	*y*	*z*
O(1)	1.354 1(16)	0.142 1(7)	0.370 3(13)
O(2)	0.853 4(19)	0.532 6(8)	−0.366 1(14)
O(3)	0.650 0(26)	0.593 7(12)	−0.348 2(17)
N(1)	0.756 9(27)	0.542 6(11)	−0.313 1(18)
N(2)	0.747 61(18)	0.402 6(8)	0.209 0(13)
N(3)	0.840 1(20)	0.386 8(8)	0.138 3(14)
N(4)	0.960 2(16)	0.338 9(7)	0.180 4(12)
N(5)	1.041 8(19)	0.263 9(8)	0.369 4(13)
N(6)	1.256 1(19)	0.181 4(9)	0.431 9(15)
C(1)	0.711 9(23)	0.486 4(11)	−0.008 1(18)
C(2)	0.688 0(25)	0.524 4(11)	−0.117 2(18)
C(3)	0.778 6(22)	0.501 5(12)	−0.190 9(16)
C(4)	0.887 6(23)	0.442 9(11)	−0.160 0(17)
C(5)	0.906 4(21)	0.406 2(9)	−0.051 0(15)
C(6)	0.820 2(21)	0.429 3(10)	0.025 1(17)
C(7)	0.801 5(23)	0.352 7(10)	0.311 2(17)
C(8)	0.669 3(24)	0.294 1(10)	0.309 5(17)
C(9)	0.675 0(30)	0.286 7(12)	0.444 0(19)
C(10)	0.745 2(30)	0.352 9(14)	0.512 9(23)
C(11)	0.850 2(25)	0.388 3(10)	0.447 3(18)
C(12)	0.951 5(22)	0.311 2(10)	0.294 3(16)
C(13)	1.158 9(26)	0.223 1(11)	0.339 5(19)
C(14)	1.186 9(24)	0.216 2(10)	0.220 7(18)
C(15)	1.312 3(23)	0.163 4(10)	0.249 1(18)
C(16)	1.403 3(26)	0.128 9(12)	0.176 3(19)

Table 7. Crystal data for compound (**4b**).

Formula	$C_{35}H_{26}Br_2N_4O$
M (daltons)	678.43
Crystal size (mm)	0.25 × 0.25 × 0.2
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.263(3)
b (Å)	11.961(3)
c (Å)	13.226(4)
α (°)	83.90(2)
β (°)	87.67(2)
γ (°)	73.37(2)
V (Å^3)	1 546.76
Z	2
D_c (g cm^{-3})	1.46
μ (cm^{-1})	25.77
F(000)	684
Radiation	Mo-K_α
Graphite monochromator	λ 0.7093 Å
Diffractometer	Hilger Y290
Orienting reflections:	
range	25; 13 < θ < 20°
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 48°
No. unique data	2 667
Total $I > 3\sigma(I)$	2 291
No. of parameters fitted	282
R^a	6.97%
$R_w{}^b$	7.43%
Quality-of-fit indicator[c]	3.7
Largest shift/esd, final cycle	< 0.002
Largest positive peak (e Å^{-3})	0.32
Largest negative peak (e Å^{-3})	−0.34

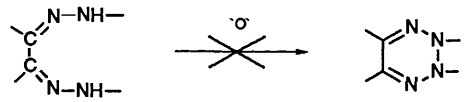
[a] $R = [\Sigma(|F_o - F_c|)]/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - 0.00057 \cdot F_o{}^2]$. [c] Quality-of-fit = $[\Sigma w - (F_o - F_c)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

give triazole products depending on the substituents. The structure (**22**), originally expected in the earlier literature, cannot adopt a boat structure.

Table 8. Crystal data for compound (**6b**).

Formula	$C_{20}H_{14}BrN_3O$
M (daltons)	392.254
Crystal size (mm)	0.35 × 0.38 × 0.25
Crystal system	Orthorhombic
Space group	*Pnma*
a (Å)	16.599(5)
b (Å)	16.876(6)
c (Å)	5.945(1)
V (Å^3)	1 665.34
Z	4
D_c (g cm^{-3})	1.57
μ (cm^{-1})	24.03
F(000)	792
Radiation	Mo-K_α
Graphite monochromator	λ 0.7093 Å
Diffractometer	Enraf-Nonius CAD4F
Orienting reflections:	
range	25; 13 < θ < 20°
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 48°
Transmission factors, max/min	1.0, 0.75
No. unique data	1 292
Total $I > 3\sigma(I)$	886
No. of parameters fitted	59
R^a	4.25%
$R_w{}^b$	3.85%
Quality-of-fit indicator[c]	2.2
Largest shift/esd, final cycle	< 0.002
Largest positive peak (e Å^{-3})	0.25
Largest negative peak (e Å^{-3})	−0.24

[a] $R = [\Sigma(|F_o - F_c|)]/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2$. [c] Quality-of-fit = $[\Sigma w - (F_o - F_c)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.



(**21**) (**22**)

Experimental

M.p.s were measured on an Electrothermal apparatus and are uncorrected. IR spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on a JEOL JNM-GX-270 instrument with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulphoxide as solvents. The substrates (**1**) were prepared as previously described.[5,17] The dipolarophile (*E*)-cinnamaldehyde was purchased from Aldrich and the *N*-sulphinylamines[18] and methyl cyanodithioformate (**7**)[19] were prepared by literature procedures. All solvents used were purified and rigorously dried by standard procedures. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser.

I. 1,3,4,5-*Oxatriazines* (**6**) *and Tetrahydro-oxazolo*[4,5-d]-1,2,3-*triazoles* (**4**).—The following are typical examples: (Nos, 3 and 1, Table 1). A solution of the dipole (**1a**) (777 mg) in dry ethyl methyl ketone (10 cm^3) was treated with (*E*)-cinnamaldehyde (0.25 cm^3) and stirred under reflux for 8 h. On cooling, compound (**4a**) 3a,5,6,6a-*tetrahydro*-2,3a,6,6a-*tetraphenyl*-5exo-*styryloxazolo*[4,5-d]-1,2,3-*triazole* separated out (883 mg, 80%), m.p. 178 °C (from Et_2O or hexane); $\delta_H(CDCl_3)$ 5.9 (1 H, d, 5-H), 6.55 (2 d, $PhCH_A{=}CH_B$), and 6.8–7.7 (22 H, m, Ar, Ph, and PhC*H*=CH) (J_{AB} 16 Hz, $J_{B\text{-}5H}$ 7.4 Hz); $\delta_C(CDCl_3)$ 91.1 (98.9,

Table 9. Crystal data for compound (**11a**).

Formula	$C_{20}H_{15}N_3S$
M (daltons)	392.42
Crystal size (mm)	0.35 × 0.40 × 0.38
Crystal system	Monoclinic
Space group	$P2_1/a$ [a]
a (Å)	8.041(2)
b (Å)	18.813(7)
c (Å)	10.884(2)
β (°)	94.90(2)
V (Å^3)	1 640.38
Z	4
D_c (g cm^{-3})	1.33
μ (cm^{-1})	1.6
F(000)	688
Radiation	Mo-K_α
Graphite monochromator	λ 0.7093 Å
Diffractometer	Enraf-Nonius CAD4F
Orienting reflections:	
range	25; 13 < θ < 20°
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 48°
No. unique data	1 981
Total $I > 3\sigma(I)$	1 045
No. of parameters fitted	127
R [a]	5.76%
R_w [b]	6.62%
Quality-of-fit indicator [c]	0.87
Largest shift/esd, final cycle	< 0.001
Largest positive peak (e Å^{-3})	0.13
Largest negative peak (e Å^{-3})	−0.14

[a] Non-standard setting of $P2_1/c$ No. 14. [b] $R = [\Sigma(|F_o - F_c|)]/\Sigma|F_o|$. [c] $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - 0.00075 \cdot F_o^2]$. [d] Quality-of-fit = $[\Sigma w - (F_o - F_c)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

Table 10. Crystal data for compound (**17b**).

Formula	$C_{26}H_{19}BrN_4$
M (daltons)	467.35
Crystal size (mm)	0.2 × 0.28 × 0.2
Crystal system	Orthorhombic
Space group	*Pnma*
a (Å)	11.649(3)
b (Å)	13.298(4)
c (Å)	13.945(3)
V (Å^3)	2 160.2
Z	4
D_c (g cm^{-3})	1.44
μ (cm^{-1})	18.57
F(000)	952
Radiation	Mo-K_α
Graphite monochromator	λ 0.710 69 Å
Diffractometer	Hilger Y290
Orienting reflections:	
range	12; 13 < θ < 20°
Temperature (° C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 48°
No. unique data	1 145
Total $I > 3\sigma(I)$	599
No. of parameters fitted	78
R [a]	6.57%
R_w [b]	6.44%
Quality-of-fit indicator [c]	3.5
Largest shift/esd, final cycle	< 0.001
Largest positive peak (e Å^{-3})	0.15
Largest negative peak (e Å^{-3})	−0.18

[a] $R = [\Sigma(|F_o - F_c|)]/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - 0.00026 \cdot F_o^2]$. [c] Quality-of-fit = $[\Sigma w - (F_o - |F_c|)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

113.4 tertiary bridgeheads), 119.8, 121.5, 123.8, 127.7, 127.74, 128.1, 128.3, 128.8, 129.2, 129.6, 129.95, 133.0, 136.9, 137.7, 139.0, 141.51, and 143.7 (see Scheme 2).

A solution of compound (**4a**) (100 mg) in ethanol (10 cm^3) was treated with acetic acid (1.0 cm^3) and the mixture was heated under reflux for 10 min or until the solution turned red. On cooling, red needles of 2,4,6-*triphenyl*-4H-1,3,4,5-*oxatriazine* (**6a**) separated out (53 mg, 90%), m.p. 171 °C (from EtOH) (*M*, cryoscopic, 310); $\delta_H(CDCl_3)$ 7.08–7.7 (12 H, m, ArH) and 8.05–8.10 (3 H, m, ArH). Full ^{13}C NMR spectrum, Scheme 2. The oxatriazines (**6**) were unreactive. When heated with aniline under reflux in *p*-xylene they cleaved to give benzanilide and gums, and when heated in aq. sodium hydroxide they decomposed to sodium benzoate. They did not react with the 4π-systems 2,3-dimethylbuta-1,3-diene and benzonitrile *N*-(*p*-nitrophenyl)imide under normal thermal conditions in hydrocarbon solvents.

II. 1,3,4,5-*Thiatriazines* (**11**).—(*a*) (No. 5, Table 1). A solution of methyl cyanodithioformate (**7**) (379 mg, 3.24 mmol) in dry benzene (50 cm^3) was added to (*Z*)-1,2-diphenyl-1,2-bis(phenylazo)ethene [the dipole (**1a**)] (1.26 g, 3.24 mmol) and the solution was stirred at ambient temperature for 1 h. Evaporation of the solvent under reduced pressure gave a red oil, which crystallized on addition of EtOH (5.0 cm^3) to give red crystals of 2,4,6-*triphenyl*-1,3,4,5-*thiatriazine* (**11a**) (890 mg, 84%), m.p. 113 °C (from MeOH); $\delta_H(CDCl_3)$ 7.15 (1 H, t, *p*-H of *N*-Ph, $J_{m,p}$ 7.4 Hz), 7.40–7.45 (8 H, m, ArH), and 7.80 (2 H, d, *ortho*-H of *N*-Ph, $J_{o,m}$ 9.0 Hz), and 8.0–8.03 (4 H, m, ArH); $\delta_C(CDCl_3)$ 140.1 (C=N), 148.4, 117.0, 130.9, and 123.9 (*N*-Ph C-1′, -2′, -3′, and -4′, respectively), and 133.6, 127.2, 128.7, and 128.8 (2- and 6-Ph C-1′, -2′, C-3′, and -4′, respectively).

(*b*) (No. 7, Table 1). An identical reaction between compounds (**7**) and (**1c**) (*Z*) 1,2-bis-(*p*-nitrophenylazo) 1,2-diphenyl ethene], gave orange crystals of 4-(p-*nitrophenyl*)-2,6-*diphenyl*-1,3,4,5-*thiatriazine* (**11c**) (86%), m.p. 193 °C (from propan-l-ol); $\delta_H(CDCl_3)$ 7.48–7.53 (6 H, m, ArH), 7.86 and 8.30 (2 d, J_{AB} 9.5 Hz, AA′BB′, *p*-$NO_2C_6H_4$), and 8.02–8.05 (4 H, m, ArH); $\delta_C(CDCl_3)$ 141.9 (C=N), 153.3, 115.5, 124.6, and 142.7 ($C_6H_4NO_2$-*p* C-1′, -2′, -3′, and C-4′, respectively), and 132.6, 126.8, 128.6, and 131.2 (2-, 6-Ph C-1′, -2′, -3′, and -4′, respectively).

When the compounds (**11**) (1 mmol) in dichloromethane were treated with MCPBA (3 mmol) and the solution was stirred for 2 h at ambient temperature the deep red or orange colours faded to pale yellow and evaporation of the solvent, after the solution had been washed successively with aq. sodium sulphite and aq. sodium carbonate, gave the known triazoles (**12**) in >95% yields. Column chromatography on alumina with compounds (**11**) also gave quantitative desulphurization to the triazoles (**12**). In a reaction between compound (**7**) (3.24 mmol) and 1,2-bis-(*p*-nitrophenylazo)cyclohexene (3.24 mmol) carried out as described for 24 h at ambient temperature, evaporation of the benzene solvent under reduced pressure gave a residue, which crystallized on treatment with ethanol (5.0 cm^3) to give 4,5,6,7-*tetrahydro*-2-(p-*nitrophenyl*)-2H-*benzo*[d]-*triazole* (**12**; RR = $[CH_2]_4$) (85%), m.p. 204–206 °C (from EtOH) (Found: C, 58.9; H, 5.0; N, 23.1. $C_{12}H_{12}N_4O_2$ requires C, 59.0; H, 4.9; N, 22.95%); $\delta_H(CDCl_3)$ 1.89–1.94 (4 H, m, 2 × CH_2), 2.80–2.8 (4 H, m, 2 × CH_2), and 8.11 and 8.29 (4 H, 2 d, J_{AB} 9.5 Hz, AA′BB′, $C_6H_4NO_2$-*p*); $\delta_C(CDCl_3)$ 22.05 and 22.94 (CH_2), 145.5, 118.1, 125.22, and 144.1 ($C_6H_4NO_2$-*p* C-1′, -2′, -3′, and -4′, respectively), and 146.1 (C-3a and -7a).

III. 1,2,3,5-*Tetrazines* (**17**) *and Triazaspiro*[4.4]*nonanes*

Table 11. Crystal data for compound (**19b**).

Formula	$C_{16}H_{16}N_6O_3$
M (daltons)	340.34
Crystal size (mm)	0.35 × 0.38 × 0.42
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.631(3)
b (Å)	18.043(4)
c (Å)	11.150(3)
β (°)	110.83(2)
V (Å^3)	1 622.90
Z	4
D_c (g cm^{-3})	1.39
μ (cm^{-1})	0.62
F(000)	712
Radiation	Mo-K_α
Graphite monochromator	λ 0.7093 Å
Diffractometer	Enraf-Nonius CAD4F
Orienting reflections:	
range	25; 13 < θ < 20°
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 44°
No. unique data	2 174
Total $I > 3\sigma(I)$	408
No. of parameters fitted	101
R^a	6.42%
$R_w{}^b$	5.15%
Quality-of-fit indicator[c]	1.2
Largest shift/esd, final cycle	< 0.001
Largest positive peak (e Å^{-3})	0.17
Largest negative peak (e Å^{-3})	−0.16

[a] $R = [\Sigma(|F_o - F_c|)]/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - 0.0062 \cdot F_o^2]$. [c] Quality-of-fit = $[\Sigma w(F_o - F_c)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

(**19**).—(*a*) (No. 8, Table 1). A solution of (*Z*)-1,2-diphenyl-1,2-bis(phenylazo)ethene [dipole (**1a**)] (1.0 g, 2.58 mmol) and *N*-sulphinylaniline (**13a**) (538 mg, 3.86 mmol) in dry benzene (15 cm^3) was stirred under reflux for 48 h, then evaporated under reduced pressure, and the residue, dissolved in dichloromethane, was placed on a flash column of silica gel (230–400 mesh ASTM). Elution with mixtures of light petroleum (b.p. 40–60 °C)–dichloromethane (9:1 v/v to 1:1 v/v) gave 2,5-*dihydro*-2,4,5,6-*tetraphenyl*-1,2,3,5-*tetrazine* (**17a**) m.p. 197 °C (from propan-l-ol) (83%); $\delta_H(CDCl_3)$ 7.12 (3 H, m), 7.34 (3 H, t), 7.67 (8 H, m), 8.0 (2 H, d), and 8.34 (4 H, m) (all Ph); $\delta_C(CDCl_3)$ 141.2 (tetrazine C-4 and -6), 146.5, 116.15, 129.2, and 128.8 (2-Ph C-1′, -2′, -3′, and -4′, respectively), 123.4, 127.0, 128.9, and 129.2 (4- and 6-Ph C-1′, -2′, -3′, and -4′, respectively), and 144.2, 117.8, 130.2, and 133.0 (5-Ph C-1′, -2′, -3′, and -4′, respectively). Excess of compound (**13a**) was recovered from the column as aniline, along with traces of compound (**1a**).

(*b*) (No. 10, Table 1). A solution of (*Z*)-1,2-diphenyl-1,2-bis(phenylazo)ethene [dipole (**1a**)] (1.0 g, 2.58 mmol) and *p*-nitro-*N*-sulphinylaniline (**13c**) (712 mg, 3.87 mmol) in dry benzene (15 cm^3) was heated under reflux for 48 h, then evaporated under reduced pressure, and the residue was chromatographed on a column as described above for compound (**17a**) to give, first, fractions containing mixtures of compounds (**17c**) and (**17a**). The combined mixtures were rechromatographed with mixtures of light petroleum spirit (b.p. 40–60 °C)–toluene (10:1 v/v ranging to 1:1 v/v as eluent. This fractionation gave compound (**17a**) (10%) along with 2,5-*dihydro*-5-(p-*nitrophenyl*)-2,4,6-*triphenyl*-1,2,3,5-*tetrazine* (**17c**) (870 mg, 78%), m.p. 246 °C (from propan-l-ol); $\delta_H(CDCl_3)$ 6.98 (2 H, d, J_{AB} 9.2 Hz), 8.09 (2 H, d) (together $C_6H_4NO_2$-*p*, AA′BB), 7.26 (3 H, m, 2-PhH$_m$, *p*), 7.62 (6 H, m, 4- and 6-Ph, H$_{m,p}$), 7.90 (3 H, m, 2-Ph, H$_{m,p}$) and 8.19 (4 H, m, 4- and 6-Ph H$_o$); $\delta_C(CDCl_3)$ 141.82 (C-4 and -6), 145.72, 115.67, 129.32, and 128.9 (2-Ph C-1′, -2′, -3′, and -4′ respectively), 124.23, 126.63, 130.83, and 131.73 (4- and 6-Ph C-1′, -2′, -3′, and -4′ respectively), and 149.44, 116.3, 125.32, and 138.05 ($C_6H_4NO_2$-*p* C-1′, -2′, -3′, and -4′, respectively).

(*c*) (No. 14, Table 1). A solution of 1,2-bis-(*p*-nitrophenylazo)cycloheptene {dipole (**1c**; RR = $[CH_2]_4$)} (1 g, 2.54 mmol) and *p*-nitro-*N*-sulphinylaniline (**13c**) (1.4 g, 7.61 mmol) in dry benzene (15 cm^3) was heated under reflux for 48 h and evaporated under reduced pressure. The residue was placed on a silica gel flash column and eluted with dichloromethane to remove excess of *p*-nitroaniline from the product, which on recovery was crystallized from ethanol to give 1,4,5,6-tetrahydro 2,5-*bis*-(p-*nitrophenyl*)-4,6-*pentano*-1,2,3,5-*tetrazine* (**17g**) (840 mg, 84%), m.p. 217 °C (from EtOH); $\delta_H(CDCl_3)$ 1.87 (m), 2.19 (m), and 2.98 (m) (together 10 H, $[CH_2]_5$), 7.58 (2 H, d), and 8.26 (2 H, d, J_{AB} 9.2 Hz) (together 2-$C_6H_4NO_2$-*p*, AA′BB′), and 7.01 (2 H, d) and 8.20 (2 H, d, J_{AB} 8.9 Hz) (together 5-$C_6H_4NO_2$-*p*, AA′BB′), and 7.01 (2 H, d) and 8.20 (2 H, d, J_{AB} 8.9 Hz) (together 5-$C_6H_4NO_2$-*p*, AA′BB′); $\delta_C(CDCl_3)$ 24.37, 31.85, and 34.7 ($[CH_2]_5$, three different carbons only), 141.3 (tetrazine C-4), 151.0, 115.7, 126.25, and 143.8 (2-$C_6H_4NO_2$-*p* C-1′, -2′, -3′, and -4′, respectively), and 146.4, 112.9, 124.9, and 143.05 (5-$C_6H_4NO_2$-*p* C-1′, -2′, -3′, and -4′, respectively).

(*d*) (No. 15, Table 1). A solution of 1,2-bis-(*p*-nitrophenylazo)cyclohexene {dipole (**1c**; RR = $[CH_2]_4$)} (1 g, 2.63 mmol) and *p*-nitro *N*-sulphinylaniline (1.9 g, 10 mmol) in dry benzene (20 cm^3) was stirred under reflux for 48 h, then evaporated to dryness, and the residue was placed on a silica gel flash column in dichloromethane. Elution with dichloromethane removed excess of *p*-nitroaniline along with decomposition products, and the main product, compound (**19a**), was recovered crude by washing of the column with ethanol. The crude sample was rechromatographed on a similar column with toluene–ethanol (15:1 v/v) as eluant to give 2-(p-*nitrophenyl*)-4-(p-*nitrophenyl-imino*)-1,2,3-*triazaspiro*[4.4]*non*-1-*en*-2-*ium*-3-*ide* (**19a**) (470 mg, 47%), m.p. 209 °C (from propan-l-ol); $\delta_H(CDCl_3)$ 2.20 (8 H, m, $[CH_2]_4$), 8.41 (2 H, d) and 8.48 (2 H, d, J_{AB} 9.16 Hz) (together 2-$C_6H_4NO_2$-*p*, AA′BB′), and 8.21 (2 H, d) and 8.98 (2 H, d, J_{AB} 9.0 Hz) (together =$NC_6H_4NO_2$-*p*, AA′BB′); $\delta_C(CDCl_3)$ 26.81 and 41.73 ($[CH_2]_2$), 87.22 (spiro C-5), 176.2 (C-4), 143.6, 123.8, 124.8, and 150.14 (2-$C_6H_4NO_2$-*p* C-1′, -2′, -3′, and -4′, respectively), and 156.1, 123.0, 124.6, and 143.5 (=$NC_6H_4NO_2$-*p* C-1′, -2′, -3′, and -4′, respectively).

IV. *X-Ray Crystal Structures*.—Atomic co-ordinates are given in Tables 2–6. Crystal data are in Tables 7–11.

The structures of compounds (**4b**), (**6b**), and (**17b**) were solved by Patterson methods, SHELX 86,[20] and refined by full-matrix least-squares using SHELX 76.[21] The structures of compounds (**11a**) and (**19b**) were solved by direct methods, SHELX 86,[20] and refined by full-matrix least-squares using SHELX 76.[21] Data were corrected for Lorentz and polarization effects but not for absorption for all structures except (**6b**), which was corrected for absorption also.[22] Hydrogen atoms were included in calculated positions with fixed thermal parameters (0.05). For compound (**19b**) all atoms were refined isotropically. For compound (**4b**) the bromine atoms, the carbon atoms of the unsubstituted phenyl groups, and C(16) and C(17) were refined anisotropically. For compound (**17b**) the bromine atom was refined anisotropically. For compound (**6b**) the bromine atom was refined anisotropically, and for compound (**11a**) the following atoms were refined anisotropically; S(1), N(1), N(2), N(3), C(1), and C(2). The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the

literature.[23,25] All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings.[26]*

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* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Tables of H-atom co-ordinates, bond lengths, and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

References

1 H. Neunhoeffer in 'Comprehensive Heterocyclic Chemistry,' series eds. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, Vol. 3 (2.21), eds. A. J. Boulton and A. McKillop, pp. 531–572; M. Sainsbury, *ibid.*, pp. 995–1038.
2 K. Kubo, T. Nonaka, and K. Odo, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1339.
3 C. Grugel and W. P. Neumann, *Liebigs Ann. Chem.*, 1979, 870.
4 G. Ege and K. Gilbert, *Tetrahedron Lett.*, 1979, 4253.
5 R. N. Butler, A. M. Evans, A. M. Gillan, J. P. James, E. M. McNeela, D. Cunningham, and P. McArdle, preceding paper.
6 Part of this work has been published in preliminary communication form: 1,3,4,5-thiatriazines, R. N. Butler, P. D. O'Shea, D. Cunningham, and P. McArdle, *J. Chem. Soc., Perkin Trans. 1 Commun.*, 1989, 371; 1,3,4,5-oxatriazines, R. N. Butler, A. M. Evans, P. McArdle, and D. Cunningham, *J. Chem. Soc., Chem. Commun.*, 1987, 1090; 1,2,3,5-tetrazines, R. N. Butler, D. Cunningham, P. McArdle, and G. A. O'Halloran, *J. Chem. Soc., Chem. Commun.*, 1988, 232.
7 G. J. Gainsford and A. D. Woolhouse, *Aust. J. Chem.*, 1980, **33**, 2447.
8 R. N. Butler, unpublished results.
9 B. B. Jarvis and G. P. Stakly, *J. Org. Chem.*, 1980, **45**, 2604.
10 N. S. Isaacs and A. H. R. Laila, *J. Chem. Res.*, 1977, (*S*) 10; (*M*) 188.
11 N. S. Isaacs and A. H. R. Laila, *Tetrahedron Lett.*, 1976, 715.
12 N. S. Isaacs, 'Physical Organic Chemistry,' Longman Scientific and Technical, Harlow, Essex, 1987, p. 692.
13 T. L. Gilchrist, 'Heterocyclic Chemistry,' Pitman, London, 1985, p. 38.
14 R. N. Butler, J. P. Duffy, P. McArdle, D. Cunningham, and G. A. O'Halloran, *J. Chem. Soc. Chem. Commun.*, 1989, 120.
15 R. R. Kostikov, A. F. Khlebnikov, and K. A. Ogloblin, *J. Org. Chem. USSR (Engl. Transl.)*, 1975, **11**, 583.
16 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
17 R. N. Butler, A. M. Gillan, J. P. James, and A. M. Evans, *J. Chem. Soc., Perkin Trans. 1*, 1989, 159.
18 R. N. Butler, G. A. O'Halloran, and L. A. Burke, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1855.
19 H. E. Simmons, D. C. Broomstrom, and R. D. West, *J. Am. Chem. Soc.*, 1962, **84**, 4756.
20 G. M. Sheldrick, SHELX 86 a Computer Program for Crystal Structure Determination, University of Goetingen, 1986.
21 G. M. Sheldrick, SHELX 76, a Computer Program for Crystal Structure Determination, University of Cambridge, England, 1976.
22 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
23 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
24 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
25 D. T. Cromer and D. J. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
26 C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report ORNL (US), 1965-3794 revised (1971).

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