A new tricyclic ring and a nitrogen–sulfur analogue of the tri-pentagon bowl: cycloaddition reactions of the unstablised 1,3,4-thiadiazolium-3-methanide 1,3-dipole: steric influences on the *endo*-effect: substituted pyrrolo[2,1-*b*]-1,3,4-thiadiazole systems: azolium 1,3-dipoles

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1,3,4-Thiadiazolium-3-methanide 1,3-dipole **6** and the 2,5-diphenyl and 2,5-dimethyl derivatives, **4** and **5**, were generated at −60 °C in dichloromethane. Cycloaddition reactions with substituted alkenes gave many new derivatives of the pyrrolo[2,1-*b*][1,3,4]thiadiazole ring system. The first examples of a bowl-shaped tricyclic nitrogen-sulfur analogue of the tripentagon bowl, a 3,4,10-triaza-6-thiatricyclo[6,3,0,$0^{3,7}$]undecane ring system were obtained from *N*-substituted maleimide dipolarophiles. The reactions displayed predominantly *endo*-stereochemistry but with decreasing size of the substituent at the incipient 7a-fusion bridgehead in the cycloaddition transition state, the extent of *exo*-cycloaddition increased. The cycloadduct *endo* : *exo* ratio was reduced from exclusively *endo* to *ca.* 2 : 1 on changing the 1,3-dipole from the 2,5-diphenyl derivative **4** to the unsubstituted case **6**. X-Ray crystal structures are reported for 2,7a-diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-methyldicarboxyimide **7a**, 2,7a-diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-phenyldicarboxyimide **9e** and 2,7a-diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-7-*endo*-carbonitrile **13**.

Our interest in examining the synthetic potential of exocyclic ylides of higher azolium systems as azole embedded 1,3-dipoles has led to a range of new heterocyclic ring systems through both cycloadditions and cycloaddition–rearrangement sequences.[1–4] Cycloadditions with these types of 1,3-dipoles necessarily cause a loss of aromaticity in the parent azole and produce a fused bicyclic system with bridgehead saturation which may or may not be stable.[1] A number of simple 5,5-bicyclic heterocycles still remain quite rare or indeed unknown. One such case is the pyrrolo[2,1-*b*][1,3,4]thiadiazole system which is missing from ring indexes. We have found two reports of limited derivatives of the ring. One is from the reaction of arylidene *N*,*N*-tetramethylene hydrazones with sulfur dichloride[5] and the second is a product thought to contain the ring from the reaction of thio-4-methoxybenzoylhydrazine with levulinic acid (4-oxopentanoic acid).[6] We have[7] generated the unstablised 1,3,4-thiadiazolium-3-methanide species **4** as an unstable intermediate at −60 °C by desilylation of the salts **1** with CsF following a literature procedure[8,9] originally developed with Schiff bases. If this 1,3-dipole were to add alkenes it should open viable routes to the pyrrolo[2,1-*b*][1,3,4]thiadiazole system allowing the wide scope for substitution which is characteristic of Huisgen 1,3-dipolar cycloaddition chemistry. The instability of the species **4** coupled with the fact that cycloadducts with alkynes were unstable and rearranged *in situ* with opening of the thiadiazole ring blocked a route to the ring using alkyne dipolarophiles.[7] Problems with the lesser reactivity of alkenes and the high molar excess required at −60 °C prevented earlier attempts at cycloadditions with these. These difficulties have been overcome and we report[10] herein a range of alkene cycloadducts all of which contain the rare pyrrolo[2,1-*b*]-[1,3,4]thiadiazole ring. The 1,3-dipole system has been extended to the derivatives **5** and the parent **6**. The decreasing size of the R group at the incipient bridgehead carbon in the cycloaddition illustrated an interesting trend on the *endo–exo* stereochemistry. There was increasing growth of the *exo*-cycloaddition for a given dipolarophile for the dipole series **4** to **6**.

Results and discussion

(i) *N*-Substituted maleimide dipolarophiles

When solutions of the salts **1**–**3** (*ca.* 1 mmol) in CH_2Cl_2 were combined with *N*-substituted maleimide dipolarophiles (5 mmol), cooled to −60 °C, treated with CsF, stirred for 5–7 days at −60 °C and worked up at ambient temperatures good yields of stable cycloadducts were obtained. The cycloadditions with the 1,3-dipole **4** could have occurred in the *endo*- or *exo*-manner to give the tricyclic products **7** or **10** respectively (Scheme 1). For the dipole **4** however the reaction was exclusively *endo* and gave the series of products **7a**–**7g** (Scheme 1, Table 1, part (i), entries 1–7). These new tricyclic rings which contain the pyrrolo[2,1-*b*][1,3,4]thiadiazole system are derivatives of a 3,4,10-triaza-6-thiatricyclo [6.3.0.$0^{3,7}$]-undecane parent structure. The bowl shaped structures are nitrogen–sulfur analogues of the tripentagon bowl-unit from which the dodecahedron is constructed.

When the size of the R substitutent in the 1,3-dipole was changed to a methyl group as in substrate **5** (from **2**) small amounts of the *exo*-isomers **11** began to appear in these reactions. The ratio of *endo* to *exo*-isomers was in the range 4–6 : 1 for this series (Table 1, entries 8–14). Further reduction of the R group to a H atom as in the parent 1,3-dipole **6** (from **3**) caused a significant increase in the *exo*-cycloaddition. For these reactions the ratio of the *endo* isomers **9** to *exo* **12** was 1–2 : 1 (Table 1, entries 15–18, Scheme 1). The stereoisomers did not interconvert under the reaction conditions. The ratios were established from direct NMR analysis of the product mixtures. The results indicate a delicate balance between the *endo*- and

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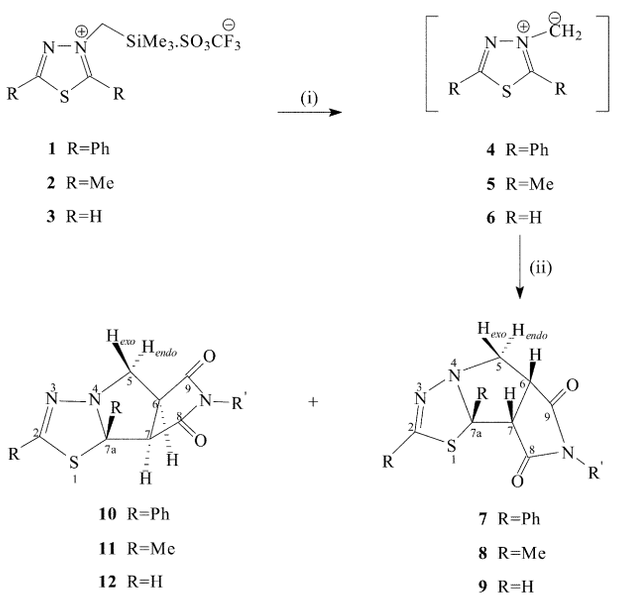
Table 1 Pyrrolo[1,2-*b*]-1,3,4-thiadiazole products

Entry	Compound or mixture no.	Mp/°C	Yield (%)	Mixture ratio *endo*/*exo*	Bridgehead signals: C-7a (δ_C) *endo* (*exo*)	Bridgehead signals: Me (or H)-7a (δ_H) *endo* (*exo*)
(i) From N-substituted maleimides						
1	**7a**	133–135	47	—	94.2	—
2	**7b**	148–149	50	—	93.4	—
3	**7c**	148–150	54	—	93.9	—
4	**7d**	174–177	40	—	94.1	—
5	**7e**	171–173	69	—	94.3	—
6	**7f**	195–196	52	—	94.2	—
7	**7g**	202–204	57	—	94.5	—
8	**8a/11a**	107–109	46	3.6 : 1	90.4 (89.1)	1.83 (1.62)
9	**8b/11b**	113–115	46	4.3 : 1	89.9 (89.5)	1.78 (1.42)
10	**8c/11c**	87–89	50	6.0 : 1	90.5 (89.8)	1.80 (1.74)
11	**8d/11d**	144–147	47	4.1 : 1	90.4 (90.4)[a]	(1.57–2.28)[b]
12	**8e/11e**	159–161	65	6.1 : 1	90.8 (89.3)	1.86 (1.74)
13	**8f/11f**	195–197	61	5.1 : 1	90.8 (89.4)	1.87 (1.67)
14	**8g/11g**	203–205	67	6.6 : 1	91.3 (91.3)[a]	1.85 (1.70)
15	**9a/12a**	104–106	68	1.1 : 1	73.8 (73.8)[a]	5.34 (5.10)
16	**9c/12c**	86–88	65	2.0 : 1	74.2 (74.5)	5.28 (5.03)
17	**9d/12d**	177–179	37	2.0 : 1	74.3 (74.6)	5.33 (5.08)
18	**9e/12e**	174–175	70	2.0 : 1	74.2 (73.8)	5.40 (5.25)
(ii) From mono- and disubstituted alkenes						
19	**13/22**	85–87	66	2.3 : 1	92.5 (92.0)	—
20	**14**	112–114	73	—	93.1	—
21	**15**	138–140	59	—	92.4	—
22	**24**	Gum	50	—	92.7	—
23	**16/25**	Gum	92	2.2 : 1	88.3 (89.4)	1.73 (1.72)
24	**17/26**	Gum	87	2.3 : 1	90.5 (88.6)	1.63 (1.63)[a]
25	**27/28**	67–68	97	1.8 : 1	90.4 (88.8)	1.81 (1.40)
26	**19/29**	Gum	79	2.0 : 1	75.7 (72.4)	5.07 (5.16)
27	**20/30**	Gum	71	3.2 : 1	74.7 (71.4)	5.17 (5.18)[a]
28	**21**	Gum	63	—	74.0	5.30
29	**32/33**	Gum	44	1 : 2.1	73.1 (75.2)	5.01 (5.48)
30	**37**	Gum	90	—	93.1	1.58
31	**39/38**	Gum	50	2.8 : 1	79.4 (81.8)	5.42 (4.93)

[a] Signals overlap. [b] overlapped with adamantyl signal.



Scheme 1 *Reagents*: (i) CsF; (ii) *N*-substituted maleimides.

exo-transitions states. These cycloaddition reactions proceed *via* 1,3-dipole HOMO control in the transition state[11] and the *endo*-stereochemistry can arise from a balance of favourable secondary orbital interactions and dipolar alignments.[12,13] The size of the R group is clearly significant in contributing to the *endo* effect. We have previously noted[4] that steric effects close to developing fused-bridgeheads can influence the *endo*/*exo* stereochemistry in cycloadditions with other azolium ylide 1,3-dipoles. The size of the N-substituent (R^1) on the *N*-substituted maleimide dipolarophile had no effect on the *endo*/*exo* stereochemistry. Hence changing this substituent through methyl, benzyl, substituted phenyl and adamantyl did not produce any *exo*-products from the dipole **4** and did not increase the *exo*-isomer from the products of the dipoles **5** and **6** (Scheme 1, Table 1).

The structures of the products were established from microanalyses, IR, ^{1}H and ^{13}C NMR spectra which showed all of the expected signals and multiplicities. For the series **7**, **8** and **9** the 5-H_{endo} proton was strongly deshielded ($\delta \approx 4.6$–4.8 ppm) relative to its geminal partner the 5-H_{exo} ($\delta \approx 3.5$ ppm). NOE difference spectra showed enhancements at the 7a-substituent from H-7, H-6 and 5-H_{exo} on the same face of the central ring thereby confirming the *endo*-structure. The mixture of *endo*–*exo* pairs (Table 1) could not be readily separated but the ratio was readily established from proton NMR integration. For the series of compound pairs **8/11** and **9/12** the proton signal of the bridgehead 7a-substituent (Me and H) was generally 0.15–0.4 ppm more shielded (towards TMS) in the *exo*-structures **11** and **12** due to the adjacent *cis*-amido group. Hence the bridgehead signals for the two isomers were well separated and could be accurately integrated. Other proton signals also gave similar ratios. In some cases it was possible to grow crystals of one of the isomers from the mixtures. X-Ray crystal structures of compounds **7a** and **9e** are shown in Fig. 1 and 2. They illustrate the interesting bowl-type structure of this tricyclic system containing three nitrogens and a sulfur. The structures have relieved strain by opening of the angles at the carbon fusion atoms. Thus the angles C(7)–C(7a)–S(1), C(7a)–C(7)–C(8) and

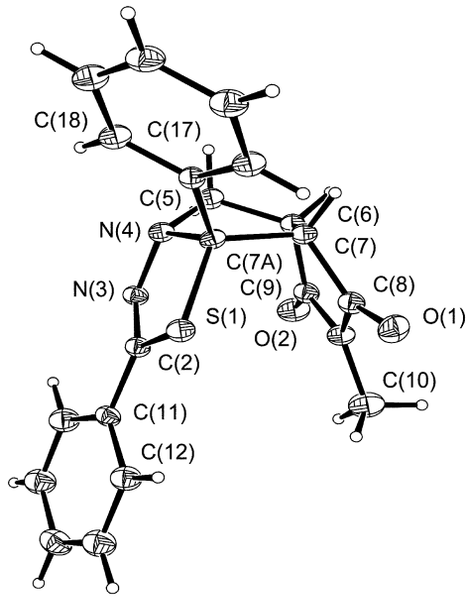


Fig. 1 X-Ray crystal structure of compound **7a**.

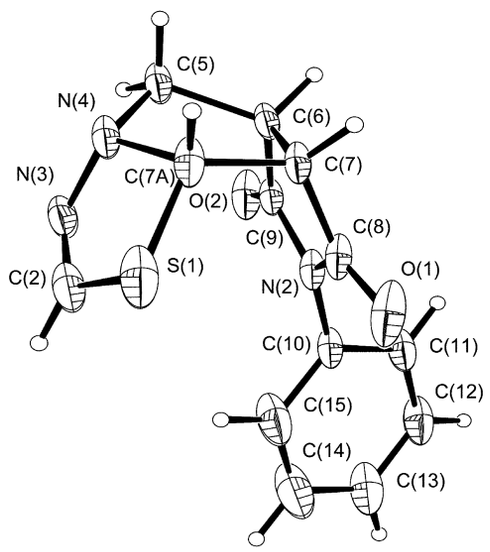
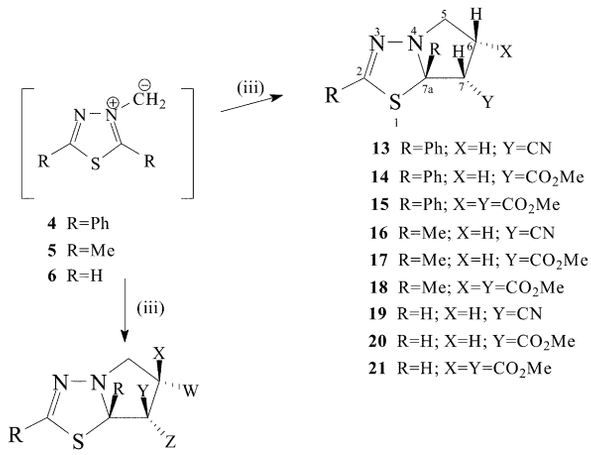


Fig. 2 X-Ray crystal structure of compound **9e**.

C(5)–C(6)–C(9) were opened to 115.4, 113.2° and 114.6° respectively for **7a** and 118.3, 115.2 and 113.4° for **9e** where the removal of the 7a-bridgehead phenyl group allows the angle at C-7a to open further. The fusion angle at the nitrogen bridgehead, C(5)–N(4)–N(3), remained relatively close to the tetrahedral value showing little opening, 110.1° for **7a** and 111.5° for **9e**.

(ii) Mono- and disubstituted alkenes

The reaction of the 1,3-dipoles **4**–**6** with acyclic alkenes led to a range of new derivatives of the pyrrolo[2,1-*b*][1,3,4]thiadiazole system (Scheme 2, Table 1, part ii). The regiochemistry was indicative of a dipole HOMO-controlled cycloaddition with the $-CH_2^-$ terminus of the dipole bonding to the unsubstituted carbon of the alkene. *endo*-Stereochemistry was dominant but generally mixtures of *endo*- and *exo*-isomers were isolated. The steric influence of the bridgehead substituent which was observed with the maleimides was not as marked with these acyclic alkenes. The structures of the products were established from NMR spectra and stereochemistry from NOE difference spectra as described. The dipole **4** with methyl acrylate gave only the *endo*-product **14** and the *exo*-isomer **23** was not



4 R=Ph
5 R=Me
6 R=H

13 R=Ph; X=H; Y=CN
14 R=Ph; X=H; Y=CO_2Me
15 R=Ph; X=Y=CO_2Me
16 R=Me; X=H; Y=CN
17 R=Me; X=H; Y=CO_2Me
18 R=Me; X=Y=CO_2Me
19 R=H; X=H; Y=CN
20 R=H; X=H; Y=CO_2Me
21 R=H; X=Y=CO_2Me

22 R=Ph; X,W,Z=H; Y=CN
23 R=Ph; X,W,Z=H; Y=CO_2Me
24 R=Ph; X=Z=CO_2Me; W=Y=H
25 R=Me; X,W,Z=H; Y=CN
26 R=Me; X,W,Z=H; Y=CO_2Me
27 R=Me; X=Z=CO_2Me; W=Y=H
28 R=Me; Y=W=CO_2Me; X=Z=H
29 R=H; X,W,Z=H; Y=CN
30 R=H; X,W,Z=H; Y=CO_2Me
31 R=H; Y=X=CO_2Me; X=W=H
32 R=H; X=Z=CO_2Me; W=Y=H
33 R=H; Y=W=CO_2Me; Z=X=H
34 R=Ph; X,W=H; Y=Me; Z=CO_2Me
35 R=Ph; X,W=H; Y=CO_2Me; Z=Me
36 R=Me; X,W=H; Y=Me; Z=CO_2Me
37 R=Me; X,W=H; Y=CO_2Me; Z=Me
38 R=H; X,W=H; Y=Me; Z=CO_2Me
39 R=H; X,W=H; Y=CO_2Me; Z=Me

Scheme 2 Reagents: (iii) mono- and disubstituted alkenes.

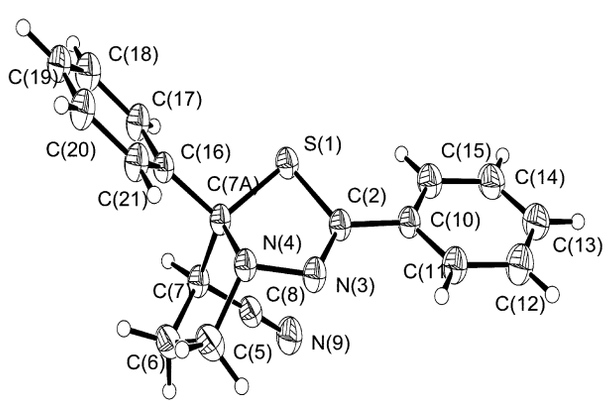


Fig. 3 X-Ray crystal structure of compound **13**.

encountered (Table 1, entry 20). In the reaction with acrylonitrile a mixture of the products **13** and **22** was formed in a 2 : 1 ratio (Table 1, entry 19). An X-ray crystal structure of compound **13** is shown in Fig. 3. Similar mixtures were obtained from the dipoles **5** and **6** (Table 1) but the unsubstituted dipole **6** with acrylonitrile gave a complicated mixture of four products which contained both regio- and stereoisomers. The regioisomers were only present in small amounts <3%. Extensive overlap of NMR signals prevented accurate assessment of the relative quantities of each isomer but the ratio of the *endo*–*exo* pair **19** and **29** was established as 2 : 1 (Table 1, entry 26). This was the only case where regioisomers were encountered. We note that other workers[14] have also encountered a mixture of all possible regio and stereo products from cycloadditions

of acrylonitrile with an azomethine methanide embedded in a fused piperidine ring.

The reactions of the dipoles **4** and **6** with dimethyl maleate and dimethyl fumarate were stereospecific. With dimethyl maleate the dipole **4** gave a single *cis*,*endo*-product, compound **15**, (Table 1, entry 21) and with dimethyl fumarate the same dipole gave a single *trans*-cycloadduct, compound **24**, where the CO_2Me at C-7 is *trans* to the bridgehead phenyl group at C-7a (Table 1, entry 22). The dipole **6** similarly gave a single *cis*,*endo* cycloadduct **21** (Table 1, entry 28) with dimethyl maleate, but with dimethyl fumarate both possible *trans*-isomers **32** and **33** were formed (Table 1, entry 29). In this case the major product was compound **33** with the CO_2Me group at C-7 in the *exo*-position reflecting the small size of the H-atom at the C-7a bridgehead. Surprisingly the dipole **5** gave an identical product mixture of the *trans*-compounds **27** and **28** (Scheme 2, Table 1, entry 25) from separate reactions with dimethyl maleate and dimethyl fumarate, thereby underlying the caution that is required in establishing stereospecificity. Clearly in this case the reaction conditions caused dimethyl maleate to isomerise to dimethyl fumarate and the result does not indicate loss of stereospecificity. Recently Huisgen *et al.*[15a] have observed a similar phenomenon in cycloadditions of *in situ* generated thiocarbonyl unsubstituted methanides with dimethyl 2,3-dicyanomaleate, where a spirothiadiazoline precursor to the 1,3-dipole caused the isomerisation of the maleate. Separate tests were carried out on dimethyl maleate under our reaction conditions in the presence of (a) CsF, (b) the salt **2** in the absence of CsF and (c) the parent 2,5-dimethyl-1,3,4-thiadiazole in an attempt to identify the agent which caused the isomerisation of dimethyl maleate. However none of these species alone changed dimethyl maleate to fumarate and this isomerisation must have occurred under the reaction conditions with the mixture of species present in the solution. When samples were taken in the first 48 h period of the 5-day reaction time NMR spectra indicated the presence of some dimethyl fumarate. We have previously noted[15b] that the phthalazinium dicyanomethanide 1,3-dipole reacts 33 times faster with dimethylfumarate than with maleate and Huisgen *et al.*[15a] have reported relative rates of 51–65 times for a number of thiocarbonyl unsubstituted methanide 1,3-dipoles with dimethyl fumarate over maleate. Hence the presence of a small equilibrium concentration of the more reactive dimethyl fumerate would account for our observation with dipole **5**.

Finally the series of 1,3-dipoles **4**–**6** were treated with a 1,1-disubstituted alkene, methyl methacrylate, in order to increase the steric requirements adjacent to the C-7a bridgehead. For normal regiochemistry with this dipolarophile either a methyl group or methoxycarbonyl group must be *cis* to the developing C-7a bridgehead substituent in the transition state. Interestingly no reaction could be induced between methyl methacrylate and the 1,3-dipole **4** involving a phenyl group at the C-7a bridgehead and neither of the products **34** or **35** were obtained. A cycloaddition readily occurred at −60 °C with the dipole **5** giving a single product **37** with the $–CO_2Me$ group *cis* to the C-7a methyl group (Table 1, entry 30). The other stereoisomer **36** was not encountered. With the dipole **6** both stereoisomers **39** and **38** of the methyl methacrylate cycloadduct were formed in the ratio 2.8 : 1 respectively (Table 1, entry 31). The stereochemistry of the products **37**–**39** was assigned by NOE difference spectra which showed enhancements from the C-7a, methyl group and H-atom to *cis* H-atoms at C-5, C-6 and the *cis* methyl group at C-7 but not to those *trans* in the *endo*-positions.

In conclusion, the 1,3,4-thiadiazolum-3-unsubstituted methanide 1,3-dipoles **4**–**6** were generated as unstable species at −60 °C in the presence of a range of substituted alkene dipolarophiles. Cycloaddition reactions opened a new route to many derivatives of the fused pyrrolo[2,1-*b*][1,3,4]thiadiazole system. Cycloadducts from *N*-substituted maleimides were derivatives of a new 3,4,10-triaza-6-thiatricyclo[6,3,0,$0^{3,7}$]-undecane ring system.

Experimental

Mps were measured on Electrothermal and Stuart Scientific melting point apparatuses. IR spectra were measured with a Perkin-Elmer Spectrum 1000 spectrophotometer and microanalysis was performed on a Perkin-Elmer Model 240 CHN analyser. NMR spectra were measured on a JEOL-GXFT 400 instrument with tetramethylsilane as internal reference and either deuteriochloroform or deuteriodichloromethane as a solvent. ^{1}H NMR assignments were supported by selective proton decoupling, COSY spectra and NOE difference spectra. H_x and H_y refer to the prochiral CH_2 of the benzyl group in compounds **7b** and **8b/11b**. *J* values are given in Hz but for some isomeric and minor products weakness of signals combined with signal overlap prevented *J* value measurements. ^{13}C NMR assignments were supported by DEPT spectra. 2,5-Dimethyl-1,3,4-thiadiazole was purchased from ACROS. The thiadiazoles were prepared as previously described.[16,17] The *N*-adamantylmaleimide was prepared according to a literature procedure.[18] The other dipolarophiles were purchased from Aldrich.

2,5-Diphenyl-3-trimethylsilylmethyl-1,3,4-thiadiazolium trifluoromethanesulfonate 1

A solution of 2,5-diphenyl-1,3,4-thiadiazole (0.5 g, 2.1 mmol) and trimethylsilylmethyl trifluoromethanesulfonate (0.46 cm^3, 2.31 mmol) in dry dichloromethane (10 cm^3) was stirred at 50 °C under a reflux condenser for 24 hours, evaporated under reduced pressure and the white residue washed with diethyl ether to give 2,5-diphenyl-3-trimethylsilylmethyl-1,3,4-thiadiazolium triflate **1**, mp 128–129 °C (from CH_2Cl_2–Et_2O) (75%) (Found: C, 48.0; H, 4.1; N, 5.7. $C_{19}H_{21}F_3N_2O_3S_2Si$ requires C, 48.0; H, 4.4; N, 5.9%); δ_H ($CDCl_3$) 0.19 (s, 9H, $SiMe_3$), 4.34 (s, 2H, N–CH_2), 7.55–7.74 (m, 6H, H_{meta}, H_{para}), 7.91–7.96 (m, 4H, H_{ortho}); δ_C ($CDCl_3$) −2.2 ($SiMe_3$), 48.9 (N–CH_2), 134.1, 130.1, 127.9, 122.1 (C-1′, C-2′, C-3′, C-4′ of C-2-Ph), 133.9, 130.1, 129.8, 126.2 (C-1′, C-2′, C-3′, C-4′ of C-5-Ph), 168.6 (C-5), 170.4 (C-2).

2,5-Dimethyl-3-trimethylsilylmethyl-1,3,4-thiadiazolium trifluoromethanesulfonate 2

A solution of 2,5-dimethyl-1,3,4-thiadiazole (0.5 g, 4.4 mmol) and trimethylsilylmethyl trifluoromethanesulfonate (0.96 cm^3, 4.83 mmol) in dry dichloromethane (10 cm^3) was stirred at 50 °C under a reflux condenser for 24 hours, evaporated under reduced pressure and the white residue washed with diethyl ether to give 2,5-dimethyl-3-trimethylsilylmethyl-1,3,4-thiadiazolium triflate **2**, mp 82–83 °C (from CH_2Cl_2–Et_2O) (95%) (Found: C, 31.0; H, 4.7; N, 7.9. $C_9H_{17}F_3N_2O_3S_2Si$ requires C, 30.9; H, 4.9; N, 8.0%); δ_H ($CDCl_3$) 0.10 (s, 9H, $SiMe_3$), 2.71 (s, 3H, Me-5), 2.90 (s, 3H, Me-2), 3.98 (s, 2H, N–CH_2); δ_C ($CDCl_3$) −2.6 ($SiMe_3$), 14.8 (Me-5), 15.8 (Me-2), 46.9 (N–CH_2), 166.0 (C-5), 171.6 (C-2).

3-Trimethylsilylmethyl-1,3,4-thiadiazolium trifluoromethanesulfonate 3

A solution of 1,3,4-thiadiazole (0.55 g, 6.4 mmol) and trimethylsilylmethyl trifluoromethanesulfonate (1.4 cm^3, 7.0 mmol) in dry dichloromethane (10 cm^3) was stirred at 50 °C under a reflux condenser for 24 hours, evaporated under reduced pressure and the white residue washed with diethyl ether to give 3-trimethylsilylmethyl-1,3,4-thiadiazolium triflate, **3**, mp 87–89 °C (from CH_2Cl_2–Et_2O) (99%) (Found: C, 26.2; H, 3.7; N, 8.7. $C_7H_{13}F_3N_2O_3S_2Si$ requires C, 26.1; H, 4.0; N, 8.7%); δ_H ($CDCl_3$) 0.21 (s, 9H, $SiMe_3$), 4.48 (s, 2H, N–CH_2), 9.78 (s, 1H, H-5),

10.63 (s, 1H, H-2); δ_C ($CDCl_3$) −3.0 ($SiMe_3$), 51.0 (N–CH_2), 158.6 (C-5), 158.7 (C-2).

(i) Reactions with maleimide dipolarophiles: *N*-methylmaleimide, *N*-benzylmaleimide, *N*-*tert*-butylmaleimide, *N*-adamantylmaleimide, *N*-phenylmaleimide, *N*-*p*-tolylmaleimide, *N*-*p*-bromophenylmaleimide

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-methyldicarboxyimide 7a. A solution of the salt **1** (0.5 g, 1.05 mmol) and *N*-methylmaleimide (0.58 g, 5.25 mmol) in CH_2Cl_2 (30 cm^3) was cooled to −60 °C, treated with CsF (0.32 g, 2.1 mmol), stirred at −60 °C for 7 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm^3) placed on a silica gel-60 column (230–400 mesh ASTM). Elution with a gradient mixture of petroleum spirit (bp 40–60 °C) and CH_2Cl_2 in the gradient 1 : 0 to 0 : 1 gave **7a**, (47%) mp 133–135 °C (EtOH) (Found: C, 66.0; H, 4.7; N, 11.5. $C_{20}H_{17}N_3O_2S$ requires C, 66.1; H, 4.7; N, 11.6%); IR ν_{max} (Nujol mull) cm^{-1} 1783, 1709 (C=O); δ_H ($CDCl_3$) 2.68 (s, 3H, N–CH_3), 3.33 (dd, 1H, H-6), 3.53 (dd, 1H, H-5_{exo}), 3.97 (d, 1H, H-7), 4.64 (dd, 1H, H-5_{endo}), 7.33–7.54 (m, 8H, $H_{aromatic}$), 7.65 (d, 2H, *J* 7.8, H_{ortho} of C-7aPh), *gem* $^2J_{5exo\text{-}5endo}$ 13.2, *vic* $^3J_{H5exo\text{-}H6}$ 7.5, *vic* $^3J_{H6\text{-}H7}$ 7.8, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 25.1 (N–Me), 46.7 (C-6), 54.9 (C-5), 58.5 (C-7), 94.2 (C-7a), 126.4, 127.1, 128.5, 128.7, 129.3 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 130.4, 140.3 (C-1′ of phenyl groups), 148.3 (C-2), 175.2, 177.4 (C=O).

Similarly obtained were compounds **7b**–**7g**.

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-benzyldicarboxyimide 7b. Compound **7b**: yield 50%, mp 148–149 °C (EtOH) (Found: C, 71.0; H, 4.7; N, 9.5. $C_{26}H_{21}N_3O_2S$ requires C, 71.1; H, 4.8; N, 9.6%); IR ν_{max} (Nujol mull) cm^{-1} 1775, 1702 (C=O); δ_H ($CDCl_3$) 3.30 (dd, 1H, H-6), 3.58 (dd, 1H, H-5_{exo}), 3.98 (d, 1H, H-7), 4.35, 4.40 (two ds, 1H each, H_x and H_y), 4.61 (d, 1H, H-5_{endo}), 7.00–7.46 (m, 13H, $H_{aromatic}$), 7.62 (d, 2H, *J* 7.7, H_{ortho} of C-7aPh), *gem* $^2J_{5exo\text{-}5endo}$ 13.3, *vic* $^3J_{H5exo\text{-}H6}$ 8.1, *vic* $^3J_{H6\text{-}H7}$ 8.4, *gem* $^2J_{Hx\text{-}Hy}$ 13.9, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 42.9 (N–CH_2), 46.3 (C-6), 54.8 (C-5), 58.4 (C-7), 93.4 (C-7a), 126.1, 127.1, 128.3, 128.6, 129.2, 130.1 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 134.9, 141.2 (C-1′ of phenyl groups), 147.7 (C-2), 174.5, 177.0 (C=O).

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-*tert*-butyldicarboxyimide 7c. Compound **7c**: yield 54%, mp 148–150 °C (EtOH) (Found: C, 68.3; H, 5.5; N, 10.2. $C_{23}H_{23}N_3O_2S$ requires C, 68.2; H, 5.7; N, 10.4%); IR ν_{max} (Nujol mull) cm^{-1} 1776, 1697 (C=O); δ_H ($CDCl_3$) 1.28 (s, 9H, N–^tBu), 3.16 (dd, 1H, H-6), 3.53 (dd, 1H, H-5_{exo}), 3.81 (d, 1H, H-7), 4.64 (dd, 1H, H-5_{endo}), 7.26 −7.60 (m, 8H, $H_{aromatic}$), 7.62 (d, 2H, *J* 7.8, H_{ortho} of C-7aPh), *gem* $^2J_{5exo\text{-}5endo}$ 13.4, *vic* $^3J_{H5exo\text{-}H6}$ 7.8, *vic* $^3J_{H6\text{-}H7}$ 8.3, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 27.9 (^tBu), 40.9 ($C(CH_3)_3$), 46.3 (C-6), 55.5 (C-5), 58.6 (C-7), 93.9 (C-7a), 126.1, 126.2, 126.9, 127.0,128.1, 128.6, 129.1, 129.2 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 130.1, 141.3 (C-1′ of phenyl groups), 147.1 (C-2), 176.0, 178.3 (C=O).

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-adamantyldicarboxyimide 7d. Compound **7d**: yield 40%, mp 174–177 °C (EtOH) (Found: C, 71.7; H, 5.8; N, 8.6. $C_{29}H_{29}N_3O_2S$ requires C, 72.0; H, 6.0; N, 8.7%); IR ν_{max} (Nujol mull) cm^{-1}1773, 1699 (C=O); δ_H ($CDCl_3$) 1.58–2.56 (m, 15H, adamantyl ring), 3.29 (dd, 1H, H-6), 3.68 (dd, 1H, H-5_{exo}), 3.94 (d, 1H, H-7), 4.81 (dd, 1H, H-5_{endo}), 7.49 −7.62 (m, 6H, $H_{meta,para}$), 7.77–7.81 (m, 4H, H_{ortho} of C-7aPh and C-2Ph), *gem* $^2J_{5exo\text{-}5endo}$ 13.2, *vic* $^3J_{H5exo\text{-}H6}$ 7.6, *vic* $^3J_{H6\text{-}H7}$ 8.3, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 29.3, 29.5, 35.7, 35.9, 38.5, 39.9 (adamantyl ring), 45.9 (C-6), 55.6 (C-5), 58.3 (C-7), 61.1 (quaternary C on adamantyl ring), 94.1 (C-7a), 126.0, 126.9, 128.0, 128.3,129.0, 129.9, 130.3 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 133.5, 141.1 (C-1′ of phenyl groups), 146.9 (C-2), 175.9, 178.2 (C=O).

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-phenyldicarboxyimide 7e. Compound **7e**: yield 69%, mp 171–173 °C (EtOH) (Found: C, 70.4; H, 4.4; N, 10.0. $C_{25}H_{19}N_3O_2S$ requires C, 70.6; H, 4.5; N, 9.9%); IR ν_{max} (Nujol mull) cm^{-1} 1716, 1709 (C=O); δ_H ($CDCl_3$) 3.48 (dd, 1H, H-6), 3.86 (dd, 1H, H-5_{exo}), 4.12 (d, 1H, H-7), 4.79 (dd, 1H, H-5_{endo}), 6.78–7.58 (m, 13H, $H_{aromatic}$), 7.69 (d, 2H, *J* 8.1, H_{ortho} of C-7aPh), *gem* $^2J_{5exo\text{-}5endo}$ 13.3, *vic* $^3J_{H5exo\text{-}H6}$ 7.7, *vic* $^3J_{H6\text{-}H7}$ 8.1, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 46.7 (C-6), 55.3 (C-5), 58.5 (C-7), 94.3 (C-7a), 126.3, 127.1, 128.4, 128.6, 128.8, 129.2, 130.2, 130.4 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 131.4, 140.2 (C-1′ of phenyl groups), 148.1 (C-2), 173.8, 176.4 (C=O).

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-*p*-tolyldicarboxyimide 7f. Compound **7f**: yield 52%, mp 195–196 °C (EtOH) (Found: C, 70.9; H, 4.8; N, 9.5. $C_{26}H_{21}N_3O_2S$ requires C, 71.1; H, 4.8; N, 9.6%); IR ν_{max} (Nujol mull) cm^{-1} 1717, 1709 (C=O); δ_H ($CDCl_3$) 2.25 (s, 3H, *p*-CH_3), 3.48 (dd, 1H, H-6), 3.62 (dd, 1H, H-5_{exo}), 4.11 (d, 1H, H-7), 4.78 (dd, 1H, H-5_{endo}), 6.65 (d, 2H, *J* 8.1, H_{meta} of *p*-tolyl ring), 6.94 (d, 2H, H_{ortho} of *p*-tolyl ring), 7.30–7.57 (m, 6H, $H_{meta,para}$ of C-2 and C-7a phenyl groups), 7.58 (d, 2H, *J* 7.0, H_{ortho} of C-2 phenyl), 7.69 (d, 2H, *J* 7.0, H_{ortho} of C-7aPh), *gem* $^2J_{5exo\text{-}5endo}$ 13.2, *vic* $^3J_{H5exo\text{-}H6}$ 7.8, *vic* $^3J_{H6\text{-}H7}$ 8.1, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 21.0 (CH_3), 46.6 (C-6), 55.2 (C-5), 58.5 (C-7), 94.2 (C-7a), 126.1, 126.3, 127.1, 128.3, 128.6, 129.1, 129.4, 130.3 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 138.5, 140.2 (C-1′ of phenyl groups), 147.9 (C-2), 173.9, 176.5 (C=O).

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-(*p*-bromophenyl)dicarboxyimide 7g. Compound **7g**: yield 57% mp 202–204 °C (EtOH) (Found: C, 59.2; H, 3.5; N, 8.2. $C_{25}H_{18}N_3O_2SBr$ requires C, 59.5; H, 3.6; N, 8.3%); IR ν_{max} (Nujol mull) cm^{-1} 1718, 1707 (C=O); δ_H ($CDCl_3$) 3.47 (dd, 1H, H-6), 3.60 (dd, 1H, H-5_{exo}), 4.11 (d, 1H, H-7), 4.77 (dd, 1H, H-5_{endo}), 6.67 (d, 2H, *J* 8.3, H_{ortho} of *p*-bromophenyl ring), 7.24 (d, 2H, H_{meta} of *p*-bromophenyl ring), 7.26–7.48 (m, 6H, $H_{meta,para}$ of C-2 and C-7a phenyl groups), 7.55 (d, 2H, *J* 7.8, H_{ortho} of C-2 phenyl), 7.68 (d, 2H, *J* 7.3, H_{ortho} of C-7aPh), *gem* $^2J_{5exo\text{-}5endo}$ 13.2, *vic* $^3J_{H5exo\text{-}H6}$ 7.8, *vic* $^3J_{H6\text{-}H7}$ 7.8, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 46.8 (C-6), 55.4 (C-5), 58.5 (C-7), 94.5 (C-7a), 122.4, 126.3, 127.1, 128.6, 128.8, 129.3, 130.5 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 131.9, 139.9 (C-1′ of phenyl groups), 148.1 (C-2), 173.4, 176.1 (C=O).

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-methyldicarboxyimide 8a and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-methyldicarboxyimide 11a. A solution of the salt **2** (0.36 g, 1.02 mmol) and *N*-methylmaleimide (0.88 g, 5.1 mmol) in CH_2Cl_2 (30cm^3) was cooled to −60 °C, treated with CsF (0.31 g, 2.04 mmol), stirred at −60 °C for 7 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm^3) placed on a silica gel-60 column (230–400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100 : 0 to 95 : 5, gave the mixture of **8a/11a** (3.6 : 1), (46%) mp 107–109 °C (CH_2Cl_2–hexane) (Found: C, 50.5; H, 5.3; N, 17.8. $C_{10}H_{13}N_3O_2S$ requires C, 50.2; H, 5.4; N, 17.6%); IR ν_{max} (Nujol mull) cm^{-1} 1765, 1692 (C=O).

8a: δ_H ($CDCl_3$) 1.83 (s, 3H, Me-7a), 1.98 (s, 3H, Me-2), 2.90 (s, 3H, N–Me), 3.25 (d, 1H, H-7), 3.37 (dd, 1H, H-6), 3.50 (dd,

1H, H-5$_{exo}$), 4.27 (dd, 1H, H-5$_{endo}$), *gem* $^2J_{5exo\text{-}5endo}$ 13.2, *vic* $^3J_{H5exo\text{-}H6}$ 7.6, *vic* $^3J_{H6\text{-}H7}$ 8.3, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 16.4 (Me-7a), 24.9 (Me-2), 28.1 (N–Me), 45.9 (C-6), 53.9 (C-5), 56.8 (C-7), 90.4 (C-7a), 147.4 (C-2), 175.2, 177.3 (C=O).

11a: δ_H ($CDCl_3$) 1.62 (s, 3H, Me-7a), 2.16 (s, 3H, Me-2), 2.98 (s, 3H, N–Me), 3.50 (m, 2H, H-5$_{exo}$ and H-6$_{endo}$ overlapping with H-5$_{exo}$ of major *endo* isomer), 3.80 (d, 1H, 7-H$_{endo}$), 3.89 (dd, 1H, H-5$_{endo}$), *vic* $^3J_{H6\text{-}H7}$ 8.8, *gem* $^2J_{H5exo\text{-}H5endo}$ 11.2, *vic* $^3J_{H5endo\text{-}H6endo}$ 8.8; δ_C ($CDCl_3$) 16.8 (Me-7a), 23.6 (Me-2), 28.1 (N–Me), 44.9 (C-6), 53.9 (C-5), 56.6 (C-7), 89.1 (C-7a), 150.7 (C-2), 174.6, 176.8 (C=O)

Similarly obtained were the isomeric pairs **8b/11b**, **8c/11c**, **8d/11d**, **8e/11e**, **8f/11f** and **8g/11g**.

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-benzyldicarboxyimide 8b and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-benzyldicarboxyimide11b. Mixture of **8b/11b** (4.3 : 1), (46%) mp 113–115 °C (CH_2Cl_2–hexane) (Found: C, 60.8; H, 5.6; N, 13.3. $C_{16}H_{17}N_3O_2S$ requires C, 61.0; H, 5.4; N, 13.3%); IR ν_{max} (Nujol mull) cm^{-1} 1768, 1698 (C=O).

8b: δ_H ($CDCl_3$) 1.38 (s, 3H, Me-7a), 1.78 (s, 3H, Me-2), 3.27 (d, 1H, H-7), 3.35 (dd, 1H, H-6), 3.48 (dd, 1H, H-5$_{exo}$), 4.32 (dd, 1H, H-5$_{endo}$), 4.48 (d, 1H, H$_x$), 4.60 (d, 1H, H$_y$), 7.26–7.42 (m, 5H, H$_{aromatic}$), *gem* $^2J_{5exo\text{-}5endo}$ 13.6, *vic* $^3J_{H5exo\text{-}H6}$ 8.2, *vic* $^3J_{H6\text{-}H7}$ 8.4, *gem* $^2J_{Hx\text{-}Hy}$ 13.9, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 15.6 (Me-7a), 28.1 (Me-2), 42.7 (N–CH_2), 46.1 (C-6), 53.8 (C-5), 56.7 (C-7), 89.9 (C-7a), 135.3 (C-1′), 128.0 (C-2′), 128.7 (C-3′), 129.3 (C-4′), 146.5 (C-2), 174.7, 177.2 (C=O).

11b: δ_H ($CDCl_3$) 1.42 (s, 3H, Me-7a), 2.13 (s, 3H, Me-2), 3.48 (m, 2H, H-6 and H-5$_{exo}$), 3.60 (d, 1H, 7-H), 3.72 (m, 1H, 5-H$_{endo}$), 4.60 (m, 2H, H$_x$ and H$_y$), 7.26–7.42 (m, 5H, H$_{aromatic}$), *vic* $^3J_{H6\text{-}H7}$ 8.8; δ_C ($CDCl_3$) 16.9 (Me-7a), 23.2 (Me-2), 42.4 (N–CH_2), 44.9 (C-6), 53.9 (C-5), 56.4 (C-7), 89.6 (C-7a), 135.5, 128.0, 128.7, 129.3 (overlapping with major isomer), 150.3 (C-2), 174.5, 176.8 (C=O).

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-*tert*-butyldicarboxyimide 8c and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-*tert*-butyldicarboxyimide 11c. Mixture of **8c/11c** (6 : 1), (50%) mp 87–89 °C (CH_2Cl_2–hexane) (Found: C, 55.1; H, 6.5; N, 14.8. $C_{13}H_{19}N_3O_2S$ requires C, 55.5; H, 6.8; N, 15.0%); IR ν_{max} (Nujol mull) cm^{-1} 1768, 1702 (C=O).

8c: δ_H ($CDCl_3$) 1.50 (s, 9H, ^{t}Bu), 1.80 (s, 3H, Me-7a), 2.03 (s, 3H, Me-2), 3.06 (d, 1H, H-7), 3.19 (dd, 1H, H-6), 3.48 (dd, 1H, H-5$_{exo}$), 4.29 (dd, 1H, H-5$_{endo}$), *gem* $^2J_{5exo\text{-}5endo}$ 13.5, *vic* $^3J_{H5exo\text{-}H6}$ 8.1, *vic* $^3J_{H6\text{-}H7}$ 8.3, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 16.6 (Me-7a), 28.0 (^{t}Bu) 29.0 (Me-2), 45.7 (C-6), 54.5 (C-5), 56.7 (C-7), 58.3 ($C(CH_3)_3$), 90.5 (C-7a), 145.9 (C-2), 175.9, 178.1 (C=O).

11c: **(some** ^{1}H and ^{13}C shifts) δ_H ($CDCl_3$) 1.57 (s, 9H, ^{t}Bu), 1.74 (s, 3H, Me-7a), 2.15 (s, 3H, Me-2), 3.30 (m, 1H, H-6), 3.52–3.62 (m, 2H, H-7 and H-5$_{exo}$), 3.8 (m, 1H, H-5$_{endo}$); δ_C ($CDCl_3$) 16.8 (Me-7a), 23.6 (Me-2), 28.0 (^{t}Bu), 44.5 (C-6), 55.6 (C-5), 56.7 (C-7), 58.6 ($C(CH_3)_3$), 89.8 (C-7a), 150.9 (C-2), 175.7, 178.1 (C=O).

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-adamantyldicarboxyimide 8d and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-adamantyldicarboxyimide 11d. Mixture of **8d/11d** (4.1 : 1), (47%) mp 144–147 °C (CH_2Cl_2–hexane) (Found: C, 63.7; H, 6.9; N, 11.3. $C_{19}H_{25}N_3O_2S$ requires C, 63.5; H, 7.0; N, 11.7%); IR ν_{max} (Nujol mull) cm^{-1} 1777, 1696 (C=O).

8d: δ_H ($CDCl_3$) 1.57–2.28 (m, 21H, Me-7a, Me-2 and adamantyl ring), 2.95 (d, 1H, H-7), 3.09 (dd, 1H, H-6), 3.38 (dd, 1H, H-5$_{exo}$), 4.15 (dd, 1H, H-5$_{endo}$), *gem* $^2J_{5exo\text{-}5endo}$ 13.5, *vic* $^3J_{H5exo\text{-}H6}$ 8.1, *vic* $^3J_{H6\text{-}H7}$ 8.3, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 16.5 (Me-7a), 24.1 (Me-2), 28.9, 29.1, 29.3 (adamantyl CH), 35.7, 36.0, 38.7, 41.2 (adamantyl), 45.3 (C-6), 54.4 (C-5), 56.3 (C-7), 60.8 (quaternary C on adamantyl ring), 90.4 (C-7a), 146.1 (C-2), 176.0, 178.2 (C=O).

11d: **(some** ^{1}H shifts) δ_H ($CDCl_3$) 1.57–2.28 (m, 21H, Me-7a, Me-2 and adamantyl ring), 3.15 (m, 1H, H-6), 3.44 (m, 2H, H-7 and H-5$_{exo}$), 3.62 (m, 1H, H-5$_{endo}$); adamantyl signals overlapped with those of the major isomer; the carbon-13 spectrum could not be observed due to signal overlap with the major isomer and signal weakness from the low concentration of the minor isomer.

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-phenyldicarboxyimide 8e and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-phenyldicarboxyimide 11e. Mixture of **8e/11e** (6.1 : 1), (65%) mp 159–161 °C (CH_2Cl_2–hexane) (Found: C, 59.6; H, 5.0; N, 13.7. $C_{15}H_{15}N_3O_2S$ requires C, 59.8; H, 5.0; N, 14.0%); IR ν_{max} (Nujol mull) cm^{-1} 1776, 1707 (C=O).

8e: δ_H ($CDCl_3$) 1.86 (s, 3H, Me-7a), 1.99 (s, 3H, Me-2), 3.36 (d, 1H, H-7), 3.47–3.57 (m, 2H, H-6 and H-5$_{exo}$), 4.46 (dd, 1H, H-5$_{endo}$), 7.21–7.47 (m, 5H, H$_{aromatic}$), *gem* $^2J_{5exo\text{-}5endo}$ 12.8, *vic* $^3J_{H6\text{-}H7}$ 7.7, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 16.4 (Me-7a), 27.9 (Me-2), 46.0 (C-6), 53.9 (C-5), 56.7 (C-7), 90.5 (C-7a), 131.5 (C-1′), 125.7 (C-2′), 128.8 (C-3′), 128.9 (C-4′), 146.3 (C-2), 173.8, 176.2 (C=O).

11e: δ_H ($CDCl_3$) 1.74 (s, 3H, Me-7a), 2.18 (s, 3H, Me-2), 3.60 (m, 2H, H-6 and 5-H$_{exo}$), 3.91 (d, 1H, H-7), 4.00 (m, 1H, 5-H$_{endo}$), 7.21–7.47 (m, 5H, H$_{aromatic}$), *vic* $^3J_{H6\text{-}H7}$ 9.2; δ_C ($CDCl_3$) 16.6 (Me-7a), 23.3 (Me-2), 44.6 (C-6), 53.9 (C-5), 56.0 (C-7), 89.3 (C-7a), 131.1 (C-1′), 126.0 (C-2′), 128.5 (C-3′), 128.8 (C-4′), 150.3 (C-2), 173.5, 175.7 (C=O).

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-*p*-tolyldicarboxyimide 8f and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-*p*-tolyldicarboxyimide 11f. Mixture of **8f/11f** (5.1 : 1), (61%) mp 195–197 °C (CH_2Cl_2–hexane) (Found: C, 60.8; H, 5.5; N, 13.1. $C_{16}H_{17}N_3O_2S$ requires C, 61.0; H, 5.4; N, 13.3%); IR ν_{max} (Nujol mull) cm^{-1} 1783, 1710 (C=O).

8f: δ_H ($CDCl_3$) 1.87 (s, 3H, Me-7a), 2.00 (s, 3H, Me-2), 2.37 (s, 3H, *p*-Me), 3.36 (d, 1H, H-7), 3.47–3.58 (m, 2H, H-6 and H-5$_{exo}$), 4.47 (dd, 1H, H-5$_{endo}$), 7.09 (d, 2H, *J* 8.4, H$_{ortho}$), 7.26 (d, 2H, H$_{meta}$), *gem* $^2J_{5exo\text{-}5endo}$ 13.2, *vic* $^3J_{H6\text{-}H7}$ 7.7, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 16.5 (Me-7a), 28.0 (Me-2), 21.0 (*p*-Me), 46.1 (C-6), 54.1 (C-5), 56.8 (C-7), 90.5 (C-7a), 138.7 (C-1′), 125.7 (C-2′), 129.7(C-3′), 129.8 (C-4′), 147.0 (C-2), 174.0, 176.4 (C=O).

11f: δ_H ($CDCl_3$) 1.67 (s, 3H, Me-7a), 2.18 (s, 3H, Me-2), 2.38 (s, 3H, *p*-Me) 3.62–3.69 (m, 2H, H-6 and 5-H$_{exo}$), 3.91 (d, 1H, H-7), 4.00 (dd, 1H, 5-H$_{endo}$), 7.14 (d, 2H, H$_{ortho}$, overlapping with major isomer), 7.29 (d, 2H, H$_{meta}$, overlapping with major isomer), *vic* $^3J_{H6\text{-}H7}$ 9.5, *gem* $^2J_{H5endo\text{-}H5exo}$ 11.9, *vic* $^3J_{H5endo\text{-}H6endo}$ 8.6; δ_C ($CDCl_3$) 16.7 (Me-7a), 21.1 (*p*-Me), 23.4 (Me-2), 44.7 (C-6), 54.1 (C-5), 56.1 (C-7), 89.4 (C-7a), 138.7 (C-1′), 129.9 (C-2′), 125.9 (C-3′), 129.5 (C-4′), 150.5 (C-2), 173.7, 176.4 (C=O).

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-(*p*-bromophenyl)dicarboxyimide 8g and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-(*p*-bromophenyl)dicarboxyimide 11g. Mixture of **8g/11g** (6.6 : 1), (67%) mp 203–205 °C (CH_2Cl_2–hexane) (Found: C, 47.2; H, 3.4; N, 10.9. $C_{15}H_{14}N_3O_2SBr$ requires C, 47.4; H, 3.7; N, 11.1%); IR ν_{max} (Nujol mull) cm^{-1} 1780, 1712 (C=O).

8g: δ_H (CD_2Cl_2) 1.85 (s, 3H, Me-7a), 1.93 (s, 3H, Me-2), 3.36 (d, 1H, H-7), 3.49–3.53 (m, 2H, H-6 and H-5$_{exo}$), 4.40 (dd, 1H, H-5$_{endo}$), 7.12 (d, 2H, *J* 8.8, H$_{ortho}$), 7.59 (d, 2H, H$_{meta}$), *gem* $^2J_{5exo\text{-}5endo}$ 12.1, *vic* $^3J_{H6\text{-}H7}$ 8.1, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C (CD_2Cl_2) 17.0 (Me-7a), 28.5 (Me-2), 47.0(C-6), (C-5 overlapping with solvent), 57.6 (C-7), 91.3 (C-7a), 128.1 (C-1′), 128.0 (C-2′), 132.4 (C-3′), 131.4 (C-4′), 146.7 (C-2), 174.0, 176.6 (C=O).

11g: δ_H (CD_2Cl_2) 1.70 (s, 3H, Me-7a), 2.14 (s, 3H, Me-2), 3.58–3.61 (m, 2H, H-6 and 5-H_{exo}), 3.91 (d, 1H, H-7), 4.00 (m, 1H, 5-H_{endo}), 7.17 (d, 2H, *J* 8.3, H_{ortho}), 7.63 (d, 2H, H_{ortho}, overlapping with major isomer), *vic* $^3J_{H6\text{-}H7}$ 9.8; δ_C (CD_2Cl_2) All signals not seen due to low concentration of minor isomer, 17.1(Me-7a), 23.5 (Me-2), 45.3 (C-6), (C-5 overlapping with solvent), 57.4 (C-7).

5,6,7,7a-Tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-methyldicarboxyimide 9a and 5,6,7,7a-tetrahydropyrrolo-[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-methyldicarboxyimide 12a. A solution of the salt **3** (0.40 g, 1.24 mmol) and *N*-methylmaleimide (0.69 g, 6.2 mmol) in CH_2Cl_2 (30 cm^3) was cooled to −60 °C, treated with CsF (0.38 g, 2.48 mmol), stirred at −60 °C for 7 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm^3) placed on a silica gel-60 column (230–400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100 : 0 to 95 : 5, gave the mixture of **9a/12a** (1.1 : 1), (68%) mp 104–106 °C (CH_2Cl_2–hexane) (Found: C, 45.2; H, 4.0; N, 19.5. $C_8H_9N_3O_2S$ requires C, 45.5; H, 4.3; N, 19.9%); IR ν_{max} (Nujol mull) cm^{-1} 1765, 1694 (C=O).

9a: δ_H ($CDCl_3$) 2.85 (s, 3H, N–Me), 3.32–3.47 (m, 2H, H-6 and H-7), 3.54 (dd, 1H, H-5$_{exo}$), 4.63 (dd, 1H, H-5$_{endo}$), 5.34 (d, 1H, H-7a), 6.96 (s, 1H, H-2), *gem* $^2J_{5exo\text{-}5endo}$ 13.6, *vic* $^3J_{H7\text{-}H7a}$ 8.3, *vic* $^3J_{H5exo\text{-}H6}$ 7.1, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 25.2 (N–Me), 45.7 (C-6), 55.3 (C-5), 56.0 (C-7), 73.8 (C-7a), 134.3 (C-2), 174.4, 177.2 (C=O).

12a: δ_H ($CDCl_3$) 2.97 (s, 3H, N–Me), 3.32–3.47 (m, 3H, H-5$_{exo}$, H-6 and H-7), 4.45 (dd, 1H, H-5$_{endo}$), 5.10 (d, 1H, H-7a), 7.24 (s, 1H, H-2), *gem* $^2J_{5exo\text{-}5endo}$ 13.9, *vic* $^3J_{H7\text{-}H7a}$ 3.9, *vic* $^3J_{H6\text{-}H5endo}$ 9.0; δ_C ($CDCl_3$) 25.0 (N–Me), 43.9 (C-6), 51.1 (C-7), 56.5 (C-5), 73.8 (C-7a), 135.3 (C-2), 175.6, 176.1 (C=O).

Similarly obtained were the isomeric pairs **9c/12c**, **9d/12d** and **9e/12e**:

5,6,7,7a-Tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-*tert*-butyldicarboxyimide 9c and 5,6,7,7a-tetrahydropyrrolo-[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-*tert*-butyldicarboxyimide 12c. Mixture of **9c/12c** (2 : 1), (65%) mp 86–88 °C (CH_2Cl_2–hexane) (Found: C, 52.1; H, 5.9; N, 16.4. $C_{11}H_{15}N_3O_2S$ requires C, 52.2; H, 5.9; N, 16.6%); IR ν_{max} (Nujol mull) cm^{-1} 1775, 1693 (C=O).

9c: δ_H ($CDCl_3$) 1.43 (s, 9H, ^{t}butyl), 3.08–3.25 (m, 2H, H-6 and H-7), 3.44 (dd, 1H, H-5$_{exo}$), 4.55 (dd, 1H, H-5$_{endo}$), 5.28 (d, 1H, H-7a), 6.91 (s, 1H, H-2), *gem* $^2J_{5exo\text{-}5endo}$ 13.6, *vic* $^3J_{H7\text{-}H7a}$ 8.3, *vic* $^3J_{H5exo\text{-}H6}$ 7.1, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 27.7 (^{t}butyl), 45.5 (C-6), 55.9 (C-5), 56.6 (C-7), 58.5 ((*C*(CH_3)$_3$), 74.2 (C-7a), 134.3 (C-2), 175.5, 178.1 (C=O).

12c: δ_H ($CDCl_3$) 1.49 (s, 9H, ^{t}butyl), 3.08–3.25 (m, 3H, H-5$_{exo}$, H-6 and H-7), 4.35 (dd, 1H, H-5$_{endo}$), 5.03 (d, 1H, H-7a), 7.15 (s, 1H, H-2), *gem* $^2J_{5exo\text{-}5endo}$ 12.9, *vic* $^3J_{H7\text{-}H7a}$ 4.9, *vic* $^3J_{H6\text{-}H5endo}$ 8.5; δ_C ($CDCl_3$) 28.1 (^{t}butyl), 43.6 (C-6), 51.0 (C-7), 56.4 (C-5), 58.6 (*C*(CH_3)$_3$), 74.5 (C-7a), 135.4 (C-2), 176.6, 177.1 (C=O).

5,6,7,7a-Tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-adamantyldicarboxyimide 9d and 5,6,7,7a-tetrahydropyrrolo-[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-adamantyldicarboxyimide 12d. Mixture of **9d/12d** (2 : 1), (37%) mp 177–179 °C (CH_2Cl_2–hexane) (Found: C, 61.4; H, 6.4; N, 12.4. $C_{17}H_{21}N_3O_2S$ requires C, 61.6; H, 6.3; N, 12.7%); IR ν_{max} (Nujol mull) cm^{-1} 1769, 1692 (C=O).

9d: δ_H ($CDCl_3$) 1.63–2.36 (m, 15H, adamantyl), 3.12–3.31 (m, 2H, H-6 and H-7), 3.50 (dd, 1H, H-5$_{exo}$), 4.61 (dd, 1H, H-5$_{endo}$), 5.33 (d, 1H, H-7a), 7.00 (s, 1H, H-2), *gem* $^2J_{5exo\text{-}5endo}$ 13.1, *vic* $^3J_{H7\text{-}H7a}$ 8.3, *vic* $^3J_{H5exo\text{-}H6}$ 7.6, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 29.3, 29.5 (adamantyl CH's), 35.9, 36.2, 38.6, 39.1, 41.5 (adamantyl CH_2's), 45.5 (C-6), 56.0 (C-5), 56.3 (C-7), 61.2 (quaternary C of adamantyl ring), 74.3 (C-7a), 134.5 (C-2), 175.8, 178.4 (C=O).

12d: δ_H ($CDCl_3$) 1.63–2.36 (m, 15H, adamantyl), 3.12–3.31 (m, 3H, H-5$_{exo}$, H-6 and H-7), 4.41 (dd, 1H, H-5$_{endo}$), 5.08 (d, 1H, H-7a), 7.20 (s, 1H, H-2), *gem* $^2J_{5exo\text{-}5endo}$ 13.2, *vic* $^3J_{H7\text{-}H7a}$ 4.9, *vic* $^3J_{H6\text{-}H5endo}$ 8.8; δ_C ($CDCl_3$) 29.3, 29.5 (adamantyl CH's), 35.9, 36.2, 38.6, 39.1, 41.5 (adamantyl CH_2's), 43.5 (C-6), 50.9(C-7), 56.8 (C-5), 61.3 (quaternary C of adamantyl ring), 74.6 (C-7a), 135.3 (C-2), 177.0, 177.3 (C=O).

5,6,7,7a-Tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-*endo*-6,7-*N*-phenyldicarboxyimide 9e and 5,6,7,7a-tetrahydropyrrolo-[2,1-*b*][1,3,4]thiadiazole-*exo*-6,7-*N*-phenyldicarboxyimide12e. Mixture of **9e/12e** (2 : 1), (70%) mp 174–175 °C (CH_2Cl_2–hexane) (Found: C, 57.1; H, 3.8; N, 15.4. $C_{13}H_{11}N_3O_2S$ requires C, 57.1; H, 4.0; N, 15.4%); IR ν_{max} (Nujol mull) cm^{-1} 1775, 1707 (C=O).

9e: δ_H ($CDCl_3$) 3.45–3.56 (m, 2H, H-6 and H-7), 3.57–3.62 (dd, 1H, H-5$_{exo}$), 4.77 (dd, 1H, H-5$_{endo}$), 5.40 (d, 1H, H-7a), 7.07 (s, 1H, H-2), *gem* $^2J_{5exo\text{-}5endo}$ 13.8, *vic* $^3J_{H7\text{-}H7a}$ 7.8, *vic* $^3J_{H5exo\text{-}H6}$ 6.6, *vic* $^3J_{H6\text{-}H5endo}$ <1; δ_C ($CDCl_3$) 46.0 (C-6), 55.9 (C-5), 56.5 (C-7), 74.2 (C-7a), 125.8 (C-2′ and C-3′), 129.2 (C-4′), 131.7 (C-1′), 134.5 (C-2), 173.3, 176.1 (C=O).

12e: δ_H ($CDCl_3$) 3.45–3.63 (m, 3H, H-5$_{exo}$, H-6 and H-7), 4.56 (m, 1H, H-5$_{endo}$), 5.25 (d, 1H, H-7a), 7.25 (s, 1H, H-2), *vic* $^3J_{H7\text{-}H7a}$ 4.9; δ_C ($CDCl_3$) 43.9 (C-6), 51.2 (C-7), 56.6 (C-5), 73.8 (C-7a), 126.3 (C-3′), 128.7 (C-4′), 129.2 (C-2′), 131.0 (C-1′), 135.5 (C-2), 174.5, 175.0 (C=O).

(ii) Reactions with alkene dipolarophiles: acrylonitrile, methyl acrylate, dimethyl maleate, dimethyl fumarate, methyl methacrylate

2,7a-Diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-7-*endo*-carbonitrile 13 and 2,7a-diphenyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-7-*exo*-carbonitrile 22. A solution of the salt **1** (0.5 g, 1.05 mmol) and acrylonitrile (0.7 cm^3, 10.5 mmol) in CH_2Cl_2 (10 cm^3) was cooled to −60 °C, treated with CsF (0.32 g, 2.1 mmol), stirred at −60 °C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm^3) placed on a silica gel-60 column (230–400 mesh ASTM). Elution with a gradient mixture of petroleum spirit (bp 40–60 °C) and CH_2Cl_2 in the gradient 1 : 0 to 0 : 1, gave the mixture of **13/22** (2.3 : 1), (66%) mp 85–87 °C (CH_2Cl_2) (Found: C, 70.6; H, 4.8; N, 14.1. $C_{18}H_{15}N_3S$ requires C, 70.8; H, 4.9; N, 13.8%); IR ν_{max} (Nujol mull) cm^{-1} 2240 (C≡N) of **13**, 2196 (C≡N) of **22**.

13: δ_H ($CDCl_3$) 2.16 (m, 2H, H-6$_{exo}$ and H-6$_{endo}$), 3.34 (m, 1H, H-5$_{exo}$), 3.59 (dd, 1H, H-7), 4.02 (m, 1H, H-5$_{endo}$), 7.13–7.49 (m, 10H, $H_{aromatic}$), *vic* $^3J_{H7\text{-}H6exo}$, $^3J_{H7\text{-}H6endo}$ 7.4,7.3; δ_C ($CDCl_3$) 29.9 (C-6), 45.3 (C-5), 54.1 (C-7), 92.5 (C-7a), 119.0 (C≡N), 125.1, 126.5, 126.9, 127.1, 128.2, 128.5, 128.8, 129.1, 130.1 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 143.2 (C-1′ of phenyl), 147.5 (C-2).

22: δ_H($CDCl_3$) 1.90 (m, 1H, H-6$_{exo}$), 2.3 (m, 1H, H-6$_{endo}$), 3.56 (m, 1H, H-5$_{exo}$, overlapping with H-7 of major *endo* isomer), 3.90 (m, 2H, 7-H and 5-H$_{endo}$); δ_C ($CDCl_3$) 27.4 (6-C), 42.9 (5-C), 53.4 (7-C), 92.0 (C-7a), 117.9 (C≡N), 125.1, 126.5, 126.9, 127.1, 128.2, 128.5, 128.8, 129.1, 130.1 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 138.7 (C-1′ of phenyl), 147.1 (C-2).

Similarly obtained were compounds **14**, **15**, and **24** from the dipolarophiles, methyl acrylate, dimethyl maleate and dimethyl fumarate respectively.

2,7a-Diphenyl-7-*endo*-methoxycarbonyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole 14. Compound **14**: yield 73%, mp 112–114 °C (EtOH) (Found: C, 67.3; H, 5.3; N, 8.2. $C_{19}H_{18}N_2O_2S$ requires C, 67.5; H, 5.3; N, 8.3%); IR ν_{max} (Nujol mull) cm^{-1} 1733 (C=O); δ_H ($CDCl_3$) 2.10 (m, 1H, H-6$_{exo}$), 2.37 (m, 1H, H-6$_{endo}$), 3.35 (m, 1H, H-5$_{exo}$), 3.70 (dd, 1H, H-7), 3.79

(s, 3H, OMe), 4.02 (m, 1H, H-5$_{endo}$), 7.25–7.57 (m, 8H, H$_{aromatic}$), 7.74 (d, 2H, *J* 7.7, H$_{ortho}$ of C-7aPh), *vic* $^3J_{H7\text{-}H6exo}$, $^3J_{H7\text{-}H6endo}$ 8.2, 8.1; δ_C ($CDCl_3$) 27.9 (C-6), 54.1 (C-5), 59.1 (C-7), 52.2 (OMe), 93.1 (C-7a), 126.0, 127.1, 128.1, 128.5,128.7 (overlapping signals of phenyl groups, C-2′, C-3′, and C-4′), 139.8, 145.4 (C-1′ of phenyl groups), 147.7 (C-2), 172.1 (C=O).

2,7a-Diphenyl-6-*endo*,7-*endo*-bis(methoxycarbonyl)-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole 15. Compound **15**: yield 59%, mp 138–140 °C (EtOH) (Found: C, 63.6; H, 5.1; N, 7.2. $C_{21}H_{20}N_2O_4S$ requires C, 63.6; H, 5.1; N, 7.1%); IR ν_{max} (Nujol mull) cm^{-1} 1718, 1685 (C=O); δ_H ($CDCl_3$) 3.21 (m, 1H, H-6$_{exo}$), 3.66, 3.73 (s, 3H each, OMe), 3.91 (d, 1H, H-7), 4.20 (m, 2H, H-5$_{exo}$ and H-5$_{endo}$), 7.32–7.50 (m, 6H, H$_{meta,para}$), 7.56–7.59 (m, 4H, H$_{ortho}$ of C-7aPh and 2-Ph), *vic* $^3J_{H6\text{-}H7}$ 7.0; δ_C ($CDCl_3$) 43.1 (6-C), 55.1 (5-C), 58.5 (7-C), 52.0, 52.2 (OMe), 92.4 (C-7a), 125.1, 125.2, 126.0, 127.2, 127.9, 128.1, 128.4, 128.5,128.8, (signals of phenyl groups C-2′, C-3′, and C-4′), 129.8, 130.2 (C-1′ of phenyl rings), 146.2 (C-2), 170.6, 170.7 (C=O).

2,7a-Diphenyl-6-*exo*,7-*endo*-bis(methoxycarbonyl)-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole 24. Compound **24**: yield 50%, a gum (recolumned crude sample) (Found: C, 63.4; H, 5.3; N, 7.5. $C_{21}H_{20}N_2O_4S$ requires C, 63.6; H, 5.1; N, 7.1%); IR ν_{max} (Nujol mull) cm^{-1} 1738 br (C=O); δ_H($CDCl_3$) 3.50 (dd, 1H, H-5$_{exo}$), 3.97 (m, 1H, H-6$_{endo}$), 3.85, 4.07 (s, 3H each, OMe), 4.33 (d, 1H, H-7), 4.54 (dd, 1H, H-5$_{endo}$), 7.51–7.63 (m, 6H, H$_{meta,para}$), 7.75–7.77 (m, 2H, H$_{ortho}$ of 2C-Ph), 7.99–8.02 (d, 2H, *J* 7.3, H$_{ortho}$ of C-7aPh), *vic* $^3J_{H7\text{-}H6}$ 9.8, *gem* $^2J_{H5exo\text{-}H\text{-}5endo}$ 12.1, *vic* $^3J_{H5endo\text{-}H6}$ 7.3; δ_C ($CDCl_3$) 46.7 (6-C), 56.0 (5-C), 62.4 (7-C), 52.3, 52.5 (OMe), 92.7 (C-7a), 126.1, 127.0, 127.9, 128.5, 128.8 (overlapping signals of phenyl groups C-2′, C-3′, and C-4′), 130.3, 133.4 (C-1′ of phenyl rings), 143.5 (C-2), 170.7, 171.9 (C=O).

2,7a-Dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-7-*endo*-carbonitrile 16 and 2,7a-dimethyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-7-*exo*-carbonitrile 25. A solution of the salt **2** (0.36 g, 1.02 mmol) and acrylonitrile (0.67 cm^3, 10.2 mmol) in CH_2Cl_2 (10 cm^3) was cooled to −60 °C, treated with CsF (0.31 g, 2.04 mmol), stirred at −60 °C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm^3) placed on a silica gel-60 column (230–400 mesh ASTM). Elution with a gradient mixture of CH_2Cl_2 and diethyl ether in the gradient 100 : 0 to 95 : 5, gave the mixture of **16/25** (2.2 : 1), a gum (92%) (Found: C, 52.9; H, 6.1; N, 23.7. $C_8H_{11}N_3S$ requires C, 53.0; H, 6.1; N, 23.2%); IR ν_{max} (Nujol mull) cm^{-1} 2242 (C≡N).

16: δ_H ($CDCl_3$) 1.73 (s, 3H, Me-7a), 1.99–2.07 (m, 1H, H-6$_{endo}$), 2.05 (s, 3H, Me-2), 2.21–2.30 (m, 1H, H-6$_{exo}$), 3.20 (dd, 1H, H-7), 3.41–3.48 (m, 1H, H-5$_{exo}$), 3.55–3.62 (m, 1H, H-5$_{endo}$), *vic* $^3J_{H7\text{-}H6exo}$, $^3J_{H7\text{-}H6endo}$ 9.2, 9.3; δ_C ($CDCl_3$) 16.6 (Me-7a), 24.3 (Me-2), 30.3 (C-6), 40.8 (C-5), 52.0 (C-7), 88.3 (C-7a), 118.7 (C≡N), 145.1 (C-2).

25: δ_H ($CDCl_3$) 1.72 (s, 3H, Me-7a), 1.99–2.07 (m, 1H, H-6$_{endo}$), 2.08 (s, 3H, Me-2), 2.21–2.30 (m, 1H, H-6$_{exo}$), 3.00 (dd, 1H, H-7), 3.41–3.48 (m, 1H, H-5$_{exo}$), 3.55–3.62 (m, 1H, H-5$_{endo}$), *vic* $^3J_{H7\text{-}H6exo}$, $^3J_{H7\text{-}H6endo}$ 8.3, 8.2, H-5$_{exo}$ and H-5$_{endo}$, H-6$_{exo}$ and H-6$_{endo}$ are overlapping in both isomers. δ_C ($CDCl_3$) 16.2 (Me-7a), 26.4 (Me-2), 29.8 (C-6), 43.5 (C-5), 53.5 (C-6), 89.4 (C-7a), 119.3 (C≡N), 147.1 (C-2).

Similarly obtained were the isomeric pairs **17/26**, **27/28** and **37** from the dipolarophiles methyl acrylate, dimethyl fumarate and methyl methacrylate respectively.

2,7a-Dimethyl-7-*endo*-methoxycarbonyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]-thiadiazole 17 and 2,7a-dimethyl-7-*exo*-methoxycarbonyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole 26. Mixture of **17/26** (2.3 : 1), a gum (87%) (Found: C, 50.4; H, 6.7; N, 13.6. $C_9H_{14}N_2O_2S$ requires C, 50.5; H, 6.5; N, 13.1%); IR ν_{max} (Nujol mull) cm^{-1} 1705 (C=O).

17: δ_H ($CDCl_3$) 1.63 (s, 3H, Me-7a), 2.10 (s, 3H, Me-2), 2.09–2.17 (m, 1H, H-6$_{exo}$), 2.42–2.49 (m, 1H, H-6$_{endo}$), 3.09 (dd, 1H, H-7), 3.51–3.55 (m, 1H, H-5$_{exo}$), 3.67–3.73 (m, 1H, H-5$_{endo}$), 3.71 (s, 3H, OMe), *vic* $^3J_{H7\text{-}H6exo}$, $^3J_{H7\text{-}H6endo}$ 8.4, 8.3; δ_C ($CDCl_3$) 16.5 (Me-7a), 24.4 (Me-2), 32.5 (C-6), 51.9 (OMe), 53.7 (C-5), 56.3 (C-7), 90.5 (C-7a), 147.9 (C-2), 171.6 (C=O).

26: δ_H ($CDCl_3$) 1.63 (s, 3H, Me-7a, overlap with major isomer), 2.09 (s, 3H, Me-2), 1.79–1.82 (m, 1H, H-6$_{exo}$), 2.25–2.33 (m, 1H, H-6$_{endo}$), 3.32 (m, 1H, H-7), 3.42–3.46 (m, 1H, H-5$_{exo}$), 3.67–3.73 (m, 1H, H-5$_{endo}$), 3.70 (s, 3H, OMe); δ_C ($CDCl_3$) 16.1 (Me-7a), 27.0 (Me-2), 29.8 (C-6), 52.2 (OMe), 55.0 (C-5), 57.4 (C-7), 88.6 (C-7a), 145.4 (C-2), 172.9 (C=O).

2,7a-Dimethyl-6-*exo*,7-*endo*-bis(methoxycarbonyl)-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole 27 and 2,7a-dimethyl-6-*endo*,7-*exo*-bis(methoxycarbonyl)-5,6,7,7a-tetrahydropyrrolo-[2,1-*b*][1,3,4]thiadiazole 28. Mixture of **27/28** (1.8 : 1), mp 67–68 °C (from 2 : 1 v/v CH_2Cl_2–hexane) (97%) (Found: C, 48.9; H, 5.7; N, 9.8. $C_{11}H_{16}N_2O_4S$ requires C, 48.5; H, 5.9; N, 10.3%); IR ν_{max} (mull) cm^{-1} 1738, 1728 (C=O).

27: δ_H ($CDCl_3$) 1.81 (s, 3H, Me-7a), 1.92 (s, 3H, Me-2), 3.09–3.15 (m, 1H, H-6), 3.32–3.35 (m, 1H, H-7), 3.60, 3.62 (s, 3H, OMe), 3.57–3.66 (m, 1H, H-5$_{exo}$), 3.76–3.80 (m, 1H, H-5$_{endo}$); δ_C ($CDCl_3$) 15.9 (Me-7a), 31.8 (Me-2), 45.2 (C-6), 52.1, 52.2 (OMe), 56.1 (C-5), 61.2 (C-7), 90.4 (C-7a), 147.3 (C-2), 170.4, 172.2 (C=O).

28: δ_H ($CDCl_3$) 1.40 (s, 3H, Me-7a), 1.99 (s, 3H, Me-2), 3.32–3.35 (m, 2H, H-6 and H-7), 3.60, 3.65 (s, 3H, OMe), 3.57–3.66 (m, 2H, H-5$_{endo}$ and H-5$_{exo}$); δ_C ($CDCl_3$) 16.6 (Me-7a), 23.4 (Me-2), 43.1 (C-6), 52.3, 52.4 (OMe), 54.6 (C-5), 57.1 (C-7), 88.8 (C-7a), 145.8 (C-2), 170.7, 172.4 (C=O).

2,7-*endo*,7a-Trimethyl-7-*exo*-methoxycarbonyl-5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole 37. Compound **37**: yield 90%, a gum (recolumned crude sample); IR ν_{max} (CCl_4) cm^{-1} 1738 (C=O).

δ_H ($CDCl_3$) 1.34 (s, 3H, Me-7), 1.58 (s, 3H, Me-7a), 1.73 (m, 1H, H-6$_{exo}$), 2.06 (s, 3H, Me-2), 2.48 (m, 1H, H-6$_{endo}$), 3.28 (m, 1H, H-5$_{exo}$), 3.43 (m, 1H, H-5$_{endo}$), 3.66 (s, 3H, OMe); δ_C ($CDCl_3$) 16.2 (Me-7), 22.0 (Me-7a), 29.1 (Me-2), 51.9 (C-6), 51.9 (OMe), 52.1 (C-5), 62.7 (C-7), 93.1 (C-7a), 145.0 (C-2), 174.7 (C=O).

5,6,7,7a-Tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-7-*endo*-carbonitrile 19 and 5,6,7,7a-tetrahydropyrrolo[2,1-*b*][1,3,4]thiadiazole-7-*exo*-carbonitrile 29. A solution of the salt 3 (0.40 g, 1.24 mmol) and acrylonitrile (0.82 cm^3, 12.4 mmol) in CH_2Cl_2 (30 cm^3) was cooled to −60 °C, treated with CsF (0.38 g, 2.48 mmol), stirred at −60 °C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm^3) placed on a silica gel-60 column (230–400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100 : 0 to 95 : 5 gave the mixture of **19/29** (2.0 : 1), a gum (79%) (Found: C, 47.0; H, 4.5; N, 27.3. $C_6H_7N_3S$ requires C, 47.1; H, 4.7; N, 27.5%); IR ν_{max} (neat) cm^{-1} 2240 (C≡N).

19: δ_H ($CDCl_3$) 1.93–2.02 (m, 2H, H-6$_{exo}$ and H-6$_{endo}$), 2.75–2.81 (m, 1H, H-7), 3.41–3.46 (m, 1H, H-5$_{exo}$), 3.87–3.93 (m, 1H, H-5$_{endo}$), 5.07 (d, 1H, H-7a), 7.03 (s, 1H, H-2), *vic* $^3J_{H7\text{-}H7a}$ 6.3; δ_C ($CDCl_3$) 27.8 (C-6), 37.6 (C-7), 53.2 (C-5), 75.7 (C-7a), 119.4 (C≡N), 133.2 (C-2).

29: δ_H ($CDCl_3$) 1.75–1.79 (m, 1H, H-6$_{exo}$), 2.10–2.20 (m, 1H, H-6$_{endo}$), 2.35–2.38 (m, 1H, H-7), 3.11–3.39 (m, 1H, H-5$_{exo}$), 3.87–3.93 (m, 1H, H-5$_{endo}$, overlap with major isomer), 5.16 (d, 1H, H-7a), 7.07 (s, 1H, H-2), *vic* $^3J_{H7\text{-}H7a}$ 7.8; δ_C ($CDCl_3$) 25.1 (C-7), 28.6 (C-6), 53.8 (C-5), 72.4 (C-7a), 118.6 (C≡N), 134.4 (C-2)

Similarly obtained were the isomeric pairs **20/30**, **21**, **33/32**, **39/38** from the dipolarophiles methyl acrylate, dimethyl maleate, dimethyl fumarate and methyl methacrylate respectively.

5,6,7,7a-Tetrahydro-7-*endo*-methoxycarbonylpyrrolo[2,1-*b*]-[1,3,4]thiadiazole 20 and 5,6,7,7a-tetrahydro-7-*exo*-methoxycarbonylpyrrolo[2,1-*b*][1,3,4]thiadiazole 30. Mixture of **20/30** (3.2 : 1), a gum (71%) (Found: C, 44.8; H, 5.6; N, 14.6. $C_7H_{10}N_2O_2S$ requires C, 45.2; H, 5.4; N, 15.0%); IR ν_{max} (neat) cm^{-1} 1731 (C=O).

20: δ_H ($CDCl_3$) 1.96–2.06 (m, 2H, H-6$_{exo}$ and H-6$_{endo}$), 2.94 (m, 1H, H-7), 3.44–3.51 (m, 1H, H-5$_{exo}$), 3.73 (s, 3H, OMe), 3.86–3.92 (m, 1H, H-5$_{endo}$), 5.17 (d, 1H, H-7a), 7.11 (s, 1H, H-2), *vic* $^3J_{H7\text{-}H7a}$ 6.3; δ_C ($CDCl_3$) 26.8 (C-6), 52.5 (C-7), 52.1 (OMe), 53.6 (C-5), 74.7 (C-7a), 133.3 (C-2), 172.9 (C=O).

30: δ_H ($CDCl_3$) 2.00–2.06 (m, 1H, H-6$_{exo}$), 2.44–2.47 (m, 1H, H-6$_{endo}$), 2.90 (m, 1H, H-7), 3.33–3.38 (m, 1H, H-5$_{exo}$), 3.71 (s, 3H, OMe), 4.13–4.18 (m, 1H, H-5$_{endo}$), 5.18 (d, 1H, overlap with major isomer), 7.13 (s, 1H, H-2); δ_C ($CDCl_3$) 39.2 (C-6), 40.7 (C-7), 51.9 (OMe), 57.0 (C-5), 71.4 (C-7a), 134.6 (C-2), 173.8 (C=O).

5,6,7,7a-Tetrahydro-6-*endo*,7-*endo*-bis(methoxycarbonyl)pyrrolo[2,1-*b*][1,3,4]thiadiazole 21. Compound **21** yield 63%, a gum (Found: C, 44.8; H, 5.0; N, 12.0. $C_9H_{12}N_2O_4S$ requires C, 44.3; H, 4.9; N, 11.5%); IR ν_{max} (neat) cm^{-1} 1735 (C=O).

21 :δ_H ($CDCl_3$) 3.05–3.17 (m, 2H, H-6 and H-7), 3.61 (s, 3H, OMe), 3.62 (s, 3H, OMe), 3.58–3.63 (m, 1H, H-5$_{exo}$), 4.08 (dd, 1H, H-5$_{endo}$), 5.30 (d, 1H, H-7a), 7.06 (s, 1H, H-2), *gem* $^2J_{H5exo\text{-}H5endo}$ 12.5, *vic* $^3J_{H5exo\text{-}H6}$ 7.6, *vic* $^3J_{H7\text{-}H7a}$ 6.3; δ_C ($CDCl_3$) 43.9 (C-6), 52.3 (C-5), 54.9, 54.9 (OMe), 56.6 (C-7), 74.0 (C-7a), 134.3 (C-2), 170.8, 171.9 (C=O).

5,6,7,7a-Tetrahydro-6-*endo*,7-*exo*-bis(methoxycarbonyl)-pyrrolo[2,1-*b*][1,3,4]thiadiazole 33 and 5,6,7,7a-tetrahydro-6-*exo*,7-*endo*-bis(methoxycarbonyl)pyrrolo[2,1-*b*][1,3,4]thiadiazole 32. Mixture of **33/32** in a 2.1 : 1 ratio respectively, a gum (44%) (Found: C, 44.0; H, 5.0; N, 11.6. $C_9H_{12}N_2O_4S$ requires C, 44.3; H, 4.9; N, 11.5%); IR ν_{max} (neat) cm^{-1} 1731 (C=O).

33: δ_H ($CDCl_3$) 3.16–3.24 (m, 1H, H-6), 3.44 (dd, 1H, H-7), 3.63, 3.65 (s, 3H, OMe), 3.59–3.68 (m, 1H, H-5$_{exo}$), 4.20 (dd, 1H, H-5$_{endo}$), 5.01 (d, 1H, H-7a), 7.01 (s, 1H, H-2), *gem* $^2J_{H5exo\text{-}H5endo}$ 13.2, *vic* $^3J_{H7\text{-}H6}$ 7.2, *vic* $^3J_{H5endo\text{-}H6}$ 4.4, *vic* $^3J_{H7\text{-}H7a}$ 7.8; δ_C ($CDCl_3$) 44.9 (C-6), 54.5 (C-5), 52.5 (2 × OMe), 56.5 (C-7), 75.2 (C-7a), 133.8 (C-2), 171.6, 172.3 (C=O).

32: δ_H ($CDCl_3$) 3.16–3.24 (m, 1H, H-6, overlap with major isomer), 3.52 (dd, 1H, H-7), 3.61, 3.62 (s, 3H, OMe), 3.59–3.68 (m, 1H, H-5$_{exo}$, overlap with major isomer), 4.20 (m, 1H, H-5$_{endo}$, overlap with major isomer), 5.48 (d, 1H, H-7a), 6.99 (s, 1H, H-2), *vic* $^3J_{H7\text{-}H6}$ 9.6, *vic* $^3J_{H7\text{-}H7a}$ 9.3; δ_C ($CDCl_3$) 44.2 (C-6), 55.0 (C-5), 52.0, 52.3 (OMe), 57.0 (C-7), 73.1 (C-7a), 135.2 (C-2), 170.3, 172.1 (C=O).

5,6,7,7a-Tetrahydro-7-*endo*-methyl-7-*exo*-methoxycarbonyl-pyrrolo[2,1-*b*][1,3,4]thiadiazole 39 and 5,6,7,7a-tetrahydro-7-*exo*-methyl-7-*endo*-methoxycarbonylpyrrolo[2,1-*b*][1,3,4]-thiadiazole 38. Mixture of **39/38** in a ratio of 2.8 : 1, a gum (50%) (Found: C, 47.7; H, 6.0; N, 13.5. $C_8H_{12}N_2O_2S$ requires C, 48.0; H, 6.0; N, 14.0%); IR ν_{max} (neat) cm^{-1} 1731 (C=O).

39: δ_H ($CDCl_3$) 1.18 (s, 3H, Me-7), 1.57–1.61 (m, 1H, H-6$_{exo}$), 2.18–2.23 (m, 1H, H-6$_{endo}$), 3.49–3.52 (m, 1H, H-5$_{exo}$), 3.60–3.63 (m, 1H, H-5$_{endo}$, overlapping with OMe), 3.63 (s, 3H, OMe), 5.42 (s, 1H, H-7a), 6.93 (s, 1H, H-2); δ_C ($CDCl_3$) 19.7 (Me), 34.9 (C-6), 52.3 (OMe), 53.1 (C-5), 51.9 (C-7), 79.4 (C-7a), 133.1 (C-2), 175.1 (C=O).

38: δ_H ($CDCl_3$) 1.29 (s, 3H, Me-7), 1.53–1.56 (m, 1H, H-6$_{exo}$), 2.00–2.03 (m, 1H, H-6$_{endo}$), 3.32–3.38 (m, 1H, H-5$_{exo}$), 3.63 (s, 3H, OMe), 3.82–3.86 (m, 1H, H-5$_{endo}$), 4.93 (s, 1H, H-7a), 6.93 (s, 1H, H-2); δ_C ($CDCl_3$) 23.4 (Me), 33.6 (C-6), 52.3 (OMe), 53.7 (C-5), 52.5 (C-7), 81.8 (C-7a), 134.3 (C-2), 175.1 (C=O).

X-Ray crystal structure determination of compound 7a †

Good quality colourless crystals of compound **7a** were grown from ethanol at ambient temperature. The crystal used for data collection had the approximate dimensions 0.50 × 0.20 × 0.20 mm. The crystal was monoclinic with the space group $P2_1/a$ and had unit cell parameters a = 12.524(2), b = 11.088(3), c = 12.935(2) Å, α = 90, β = 99.75(2), γ = 90°. Reflections were collected on an Enraf-Nonius CAD4F four circle diffractometer, using graphite monochromated Mo–Kα radiation, λ = 0.71069Å. The criterion which qualified a reflection for observation was $I > 2\sigma(I)$ and 2370 reflections satisfied this condition. The calculated density was 1.364 Mg m^{-3} and Z = 4. The absorption coefficient was 0.203 mm^{-1} and the θ range for data collection was 2.43 to 21.98°. The total number on independent reflections was 2164 [R(int) = 0.0228]. The structure was solved by direct methods SHELXS-86,[19] and refined by full matrix least squares using SHELXS-97.[20] SHELX operations were automated using ORTEX which was also used to obtain the drawings.[21] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. After full matrix refinement the final R indices [$I > 2\sigma(I)$] were R_1 = 4.22% and wR_2 = 8.59%.

X-Ray crystal structure determination of compound 9e ‡

Good quality colourless crystals of compound **9e** were grown from CH_2Cl_2–hexane (2 : 1 v/v) at ambient temperature. The crystal used for data collection had the approximate dimensions 0.45 × 0.40 × 0.18 mm. The crystal was triclinic with the space group $P\bar{1}$ and had unit cell parameters a = 10.537(2), b = 11.710(4), c = 12.259(2) Å, α = 117.58(2), β = 99.77 (10), γ = 99.90(2)°. Reflections were collected on an Enraf-Nonius CAD4F four circle diffractometer, using graphite monochromated Mo–Kα radiation, λ = 0.71069Å. The criterion which qualified a reflection for observation was $I > 2\sigma(I)$ and 5814 reflections satisfied this condition. The calculated density was 1.434 Mg m^{-3} and Z = 4. The absorption coefficient was 0.257 mm^{-1} and the θ range for data collection was 1.96 to 21.21°. The total number on independent reflections was 2577 [R(int) = 0.0250]. The structure was solved by direct methods SHELXS-86,[19] and refined by full matrix least squares using SHELXS-97.[20] SHELX operations were automated using ORTEX which was also used to obtain the drawings.[21] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. After full matrix refinement the final R indices [$I > 2\sigma(I)$] were R_1 = 3.68% and wR_2 = 8.86%.

X-Ray crystal structure determination of compound 13 §

Good quality colourless crystals of compound **13** were grown from CH_2Cl_2 at ambient temperature (slow evaporation gave crystals suitable for X-Ray crystallographic analysis). The crystal used for data collection had the approximate dimensions

† CCDC reference number 169186. See http://www.rsc.org/suppdata/p1/b2/b208544p/ for crystallographic files in .cif or other electronic format.

‡ CCDC reference number 194667. See http://www.rsc.org/suppdata/p1/b2/b208544p/ for crystallographic files in .cif or other electronic format.

§ CCDC reference number b197666. See http://www.rsc.org/suppdata/p1/b2/b208544p/ for crystallographic files in .cif or other electronic format.

0.36 × 0.32 × 0.15 mm. The crystal was monoclinic with the space group $P2_1/c$ and had unit cell parameters $a = 12.4385(19)$, $b = 6.0956(11)$, $c = 20.623(4)$ Å, $\beta = 102.514(13)°$. Reflections were collected on an Enraf-Nonius CAD4F four circle diffractometer, using graphite monochromated Mo–Kα radiation, $\lambda = 0.71069$Å. The criterion which qualified a reflection for observation was $I > 2\sigma(I)$ and 6229 reflections satisfied this condition. The calculated density was 1.329 Mg m^{-3} and $Z = 4$. The absorption coefficient was 0.212 mm^{-1} and the θ range for data collection was 2.02 to 21.22°. The total number on independent reflections was 1642 [R(int) = 0.0361]. The structure was solved by direct methods SHELXS-86,[19] and refined by full matrix least squares using SHELXS-97.[20] SHELX operations were automated using ORTEX which was also used to obtain the drawings.[21] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. After full matrix refinement the final R indices [$I > 2\sigma(I)$] were $R_1 = 3.54\%$ and $wR_2 = 8.31\%$.

References

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