Synthesis and structures of pyrroles fused with rigid bicyclic ring systems at β-positions †

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Pyrroles fused with bicyclo[2.2.2]octene and bicyclo[2.2.1]heptene frameworks are prepared by a modified Barton–Zard method. Structures of these pyrroles and thermal behaviours of the former pyrroles are studied by X-ray and DSC analyses.

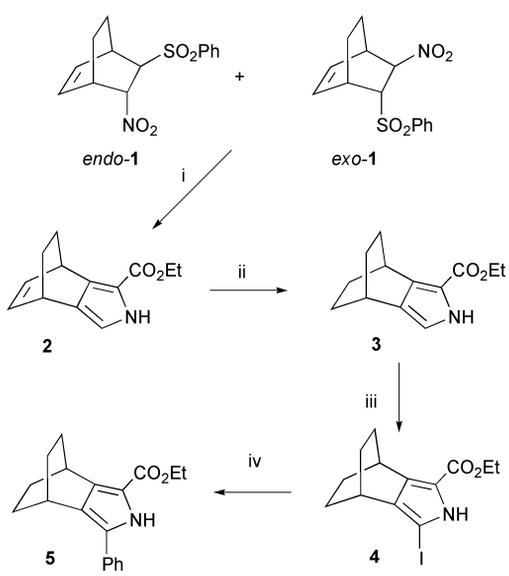
Introduction

Aromatic compounds fused with a rigid bicyclic skeleton have attracted much attention from both theoretical and synthetic points of view. Various kinds of such compounds have been prepared in order not only to build up highly conjugated aromatic systems[1] and cage compounds[2] but also to exemplify the transannular,[3] bond-alternating,[4] and radical-cation-stabilizing[5] effects. These effects are closely related to the strained nature of these compounds and have been successfully discussed in connection with their X-ray structures. For example, a bond alternation of ≈5 pm was observed for furan-fused 10b,10c-dimethyl-10b,10c-dihydropyrene at the 1,2-positions and the ring current decreased by 16–17%.[6] During the course of our investigation of the modification of electronic properties of polypyrroles and porphyrins, we have also been interested in pyrroles fused with rigid bicycloalkenes at β-positions of pyrroles.[7] In order to understand reactivity and electronic properties of the pyrroles, we have prepared various kinds of such compounds. In this paper, syntheses as well as X-ray and thermal analyses of the pyrroles will be described.

Results and discussion

Preparation of ethyl 4,7-ethano-2*H*-isoindole-1-carboxylates

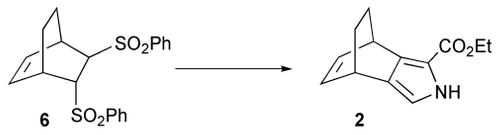
First, we focused our attention on preparing pyrroles fused with bicyclo[2.2.2]octenes (Scheme 1). The known Diels–Alder adduct **1**[8] was chosen as the starting material of a nitro-olefin equivalent in the Barton–Zard pyrrole synthesis,[9] because the corresponding α,β-unsaturated nitro and sulfonyl compounds were thought to be too unstable to undergo a retro-Diels–Alder reaction.[10] Treatment of **1** with ethyl isocyanoacetate and DBU in THF brought about the Barton–Zard reaction of 2-nitrobicyclo[2.2.2]octa-2,5-diene generated *in situ* by the elimination of phenylsulfinate, promptly to give the desired ethanoisoindole **2** in good yield,[11] and no formation of nitrobenzene was detected. The double bond of **2** was easily hydrogenated under an atmospheric pressure of hydrogen to give a partially saturated derivative **3** in quantitative yield. Iodination[12] of **3** with I_2 and HIO_3 gave α-iodo derivative **4** in 97% yield. The iodide **4** smoothly reacted with phenylboronic acid under the Suzuki coupling conditions[13] to give α-phenyl derivative **5** in 86% yield.



Scheme 1 *Reagents and conditions*: i) $CNCH_2CO_2Et$, DBU, THF, rt; ii) H_2, Pd/C, THF, rt; iii) I_2, HIO_3, MeCN; iv) $PhB(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, rt.

One possible drawback in the preparation of **2** is the rather tedious preparation of **1**. We have also reported that α,β-unsaturated sulfones can be employed for the nitro-olefins in the Barton–Zard pyrrole synthesis.[14] The known bis-sulfone **6**[15] was thought to be a promising substitute for **1**. The bis-sulfone **6** was treated with ethyl isocyanoacetate and potassium *tert*-butoxide at room temperature to give the desired pyrrole **2** in 92% yield [equation (1)] as well as a small amount of diphenyl sulfone. Contrary to the reaction of **1**, retro-Diels–Alder reaction of the intermediary bicyclo[2.2.2]octadienyl sulfone partially occurred in this case. This difference could be understood by the substituent effect on the retro-Diels–Alder reaction of adducts of 9,10-disubstituted anthracene derivatives with ethyl acrylate.[16]

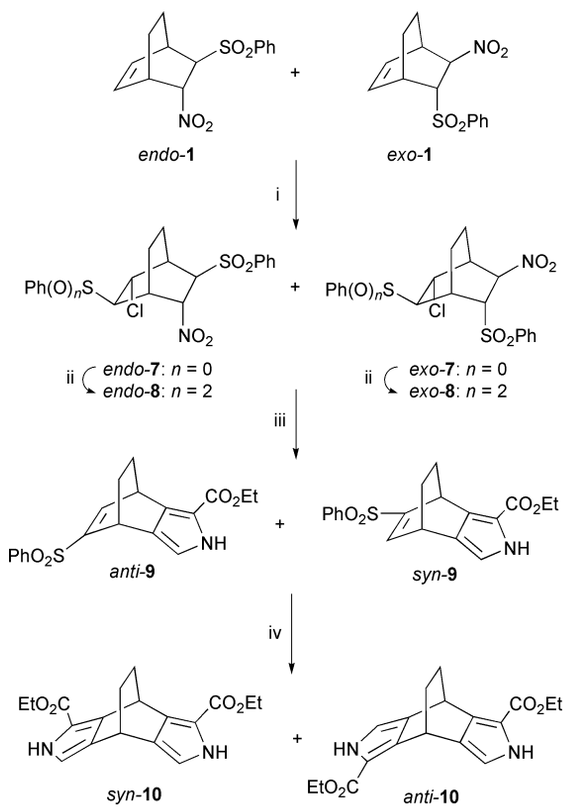
† Experimental details of compounds **2**, **3**, **4**, **5**, **14**, **15** and **26**, and Ortep drawings of compounds **2**, **4**, **5**, *anti*-**10**, **14**, **15**, **19** and *syn*-**23** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b006584f/



(1)

Preparation of diethyl 2,4,6,8-tetrahydro-4,8-ethanobenzo[1,2-*c*:4,5-*c*′]dipyrrole-1,5-dicarboxylates

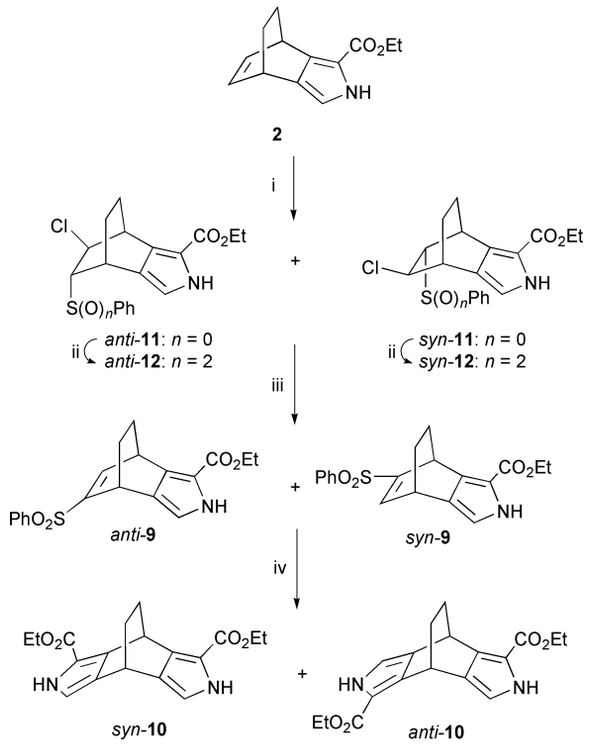
Compounds which consist of two pyrrole rings fused with rigid bicycloalkadienes at their β-positions are of considerable interest because these compounds would be promising precursors for spatially fixed porphyrin arrays.[17] First, we intended to convert the double bond of the adduct **1** to an α,β-unsaturated sulfone moiety according to the reported protocol (Scheme 2).[18]



Scheme 2 *Reagents and conditions*: i) PhSCl, CH_2Cl_2, 0 °C; ii) MCPBA, CH_2Cl_2, rt; iii) $CNCH_2CO_2Et$, DBU, THF, rt; iv) $CNCH_2CO_2Et$, $KOBu^t$, THF, rt.

Addition of benzenesulfenyl chloride to a diastereomeric mixture of **1** (*endo*/*exo* = 3/2) occurred smoothly at −78 °C to give a mixture of two isomers **7** (*endo*/*exo* = 3/2) in 83% yield. The stereochemistry of **7** was determined by NOE experiments. In this reaction, the phenylthio group only attacked the double bond of **1** from the *exo* face. Oxidation of **7** (*endo*/*exo* = 3/2) with MCPBA afforded **8** (*endo*/*exo* = 3/2) in 94% yield. Double pyrrole formation of **8** was then attempted. However, the reaction of **8** with ethyl isocyanoacetate (2.2 equiv.) and potassium *tert*-butoxide (4.4 equiv.) gave an isomeric mixture of monopyrrole **9** (41%) in a ratio of *anti*/*syn* = 3/2. The isomers *anti*-**9** and *syn*-**9** were separated by column chromatography, and the structures were confirmed by NOE experiments. Reactions of *anti*-**9** and *syn*-**9** with ethyl isocyanoacetate gave the target compounds benzodipyrroles *syn*-**10** and *anti*-**10** in 81% and 78% yield, respectively.

The double bond of **2** was also utilized for construction of another pyrrole ring. Thus, the pyrrole **2** was treated with 1.2 mole equivalents of benzenesulfenyl chloride at −78 °C to give a regioisomeric mixture of adducts **11** (81%; Scheme 3) in addition to the α-phenylthio-substituted pyrrole (19%). The



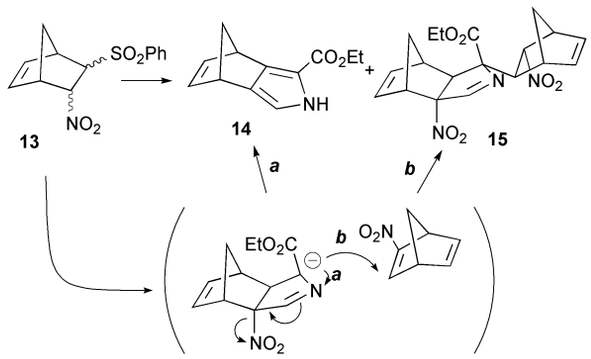
Scheme 3 *Reagents and conditions*: i) PhSCl, CH_2Cl_2, 0 °C; ii) MCPBA, CH_2Cl_2, rt; iii) DBU, CH_2Cl_2, rt; iv) $CNCH_2CO_2Et$, $KOBu^t$, THF, rt.

by-product formation was simply avoided by careful addition of one mole equivalent of benzenesulfenyl chloride at −78 °C and the target molecule **11** was obtained in quantitative yield. From NOE experiments, the phenylthio group was confirmed to occupy the *endo* position in both isomers of **11**, and the isomeric ratio of **11** was determined as *anti*/*syn* = 4/3. The isomeric mixture of **11** was converted to a mixture of the α,β-unsaturated sulfones **9** (*anti*/*syn* = 4/3) in 87% yield by oxidation with MCPBA followed by treatment of the intermediate chloro sulfones **12** with DBU.

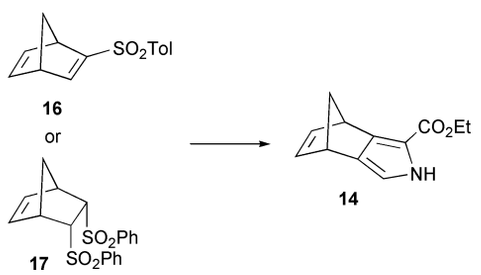
Preparation of ethyl 4,7-dihydro-4,7-methano-2*H*-isoindole-1-carboxylate 14

The reaction of nitro-olefin equivalent **13**[8] with ethyl isocyanoacetate gave the target 4,7-dihydro-4,7-methano-*2H*-isoindole **14** in rather low yield (61%; Scheme 4). Careful inspection of the reaction mixture revealed the presence (≈3%) of a by-product, NMR and IR spectra of which showed the presence of one ethyl ester, two nitro and two bicyclo[2.2.2]-heptene moieties. The structure of the by-product was finally determined as **15** by X-ray analysis. As this type of side reaction was not observed in the pyrrole-forming reactions of bicyclo-[2.2.2]octene derivatives **1**, **8** and **9**, unfavourable sp^2 hybridization in the bicyclo[2.2.1]heptene framework would retard the elimination of a nitrite anion from an anionic intermediate leading to pyrrole-ring formation (path **a**), and the Michael-type addition to another nitronorbornadiene to give **15** would compete (path ***b***).

In order to improve the yield of **14**, we employed tosylnorbornadiene **16**[18] and bis(phenylsulfonyl)norbornene **17**[15] as the starting material. The reactions of **16** and **17** with ethyl isocyanoacetate were smoothly promoted by potassium *tert*-butoxide to give the desired pyrrole **14** in 60% and 56% yield, respectively [equation (2)]. No isolable by-product was obtained in these reactions. Difference between the reactions of nitro and sulfonyl compounds would depend on the balance between nucleofugal and electron-withdrawing natures of nitro and sulfonyl groups.



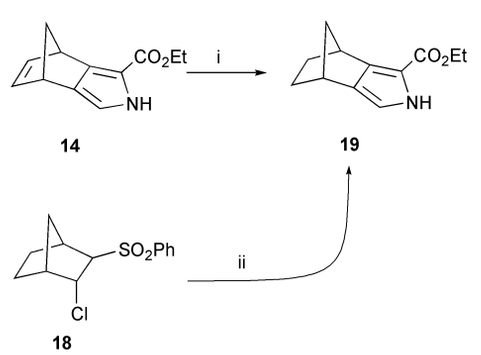
Scheme 4



(2)

Preparation of ethyl 4,5,6,7-tetrahydro-4,7-methano-2*H*-isoindole-1-carboxylate 19

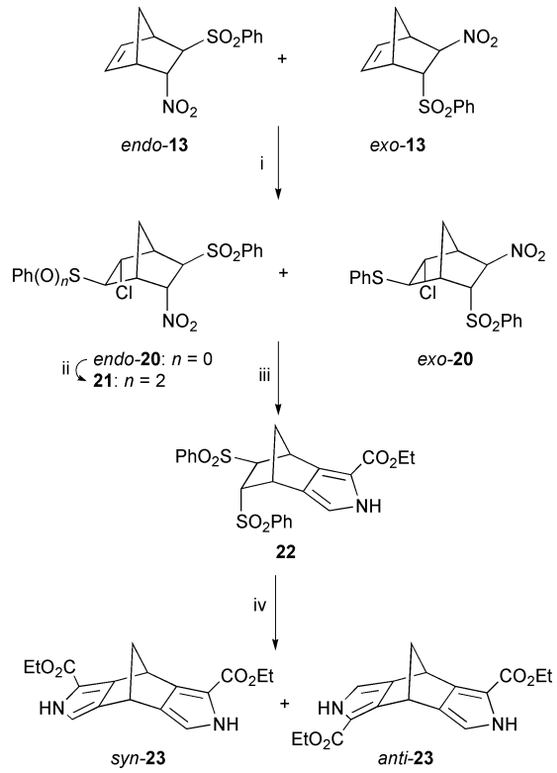
Hydrogenation under the usual conditions (an atmospheric pressure of H_2, Pd/C, THF) of **14** gave **19** only in 20% yield, and no by-product could be identified by NMR analysis of the reaction mixture. As a certain strain on the norbornadienyl skeleton might promote hydrogenolysis of the skeleton, we decided to prepare the norbornene skeleton first and then to form the pyrrole ring. Thus, the known sulfone **18**[19] was treated with ethyl isocyanoacetate and 2.4 mole equivalents of potassium *tert*-butoxide to give the pyrrole **19** in 95% yield (Scheme 5).



Scheme 5 *Reagents and conditions*: i) H_2, Pd/C, THF, rt; ii) $CNCH_2CO_2Et$, KOBu′, THF, rt.

Preparation of diethyl 2,4,6,8-tetrahydro-4,8-methanobenzo[1,2-*c*:4,5-*c*′]dipyrroledicarboxylates 23

As complete rearrangement was reported to occur in the reaction of arenesulfenyl chlorides with norbornadiene-fused pyrroles,[3b] we chose the adduct **13**[8] as the starting material (Scheme 6). A stereoisomeric mixture (*endo*/*exo* = 2/1) of **13** was treated with PhSCl. Contrary to the results with **1** described above, no reaction was observed at −78 °C. Even at room temperature for 48 h, only about half of the starting material **13** was consumed and a single isomer of **20** was obtained in 53% yield. NOE experiments revealed the obtained isomer was *endo*-**20**. The starting material **13** almost disappeared after 2 weeks and an isomeric mixture of *endo*- and *exo*-**20** (*endo*/*exo* = 5/2) was obtained in 73% yield. Extreme retardation for the addition must be due to the lowered HOMO



Scheme 6 *Reagents and conditions*: i) PhSCl, CH_2Cl_2, rt; ii) MCPBA, $CHCl_3$, rt; iii) $CNCH_2CO_2Et$, DBU, MeCN, 55 °C; iv) $CNCH_2CO_2Et$, KOBu′, THF, 55 °C.

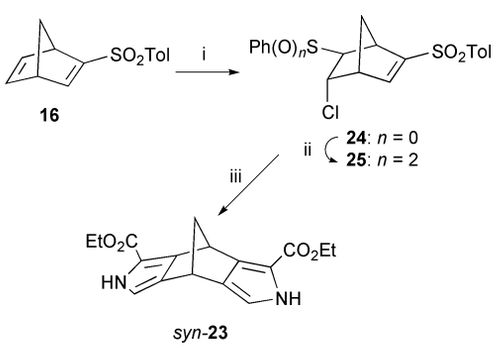
energy level of the π-bond by transannular effects of the strongly electron-withdrawing groups at the *exo* position.[20] In *exo*-**13**, a low lying $\sigma^*_{C\text{-}N(nitro)}$ orbital can effectively interact with the remote π orbital in a through-space fashion[21] and this greatly decreases the HOMO level, while the $\sigma^*_{C\text{-}S(sulfone)}$ orbital can do the same in *endo*-**13**. The pure *endo*-**20** was oxidized with MCPBA to give **21** in quantitative yield. In the reaction of **21** with ethyl isocyanoacetate under the usual conditions (DBU, THF, rt), the desired pyrrole formation was not observed and an intractable mixture was formed. When the same reaction was carried out by using DBU in acetonitrile at 55 °C, the bis-phenylsulfonylated pyrrole **22** was obtained as a single isomer in 15% yield. The stereochemistry of **22** was determined by NOE experiments. Since DBU was not basic enough to epimerize a carbon bearing a sulfonyl group, no isomerization of **22** could be expected. Formation of **22** could be rationalized by the *exo* attack of a phenylsulfinate anion on an intermediary α,β-unsaturated sulfone (like *anti*-**9**), which would be derived from *endo*-**20**, followed by protonation from the *exo* face. Another pyrrole ring formation on **22** with ethyl isocyanoacetate was performed under more severe conditions (potassium *tert*-butoxide, THF, 55 °C) to give an isomeric mixture of **23** (*anti*/*syn* = 1/5) in 50% yield.

Another route to **23** was examined by starting with the norbornadienyl sulfone **16**.[19] Addition of benzenesulfenyl chloride to **16** smoothly occurred at −78 °C to give adduct **24** as a single isomer in quantitative yield (Scheme 7). The stereochemistry of **24** was determined as an isomer bearing the *exo*-phenylthio group at the *syn* position by NOE experiments. This stereochemical selectivity was qualitatively understood by considering cationic intermediates derived from the *exo* attack of a phenylthio cation (Fig. 1): In the *syn* intermediate (left), hyperconjugative stabilization of the cationic center from the olefinic carbon was expected, while in the *anti* intermediate (right) such stabilization from the carbon bearing the sulfonyl group was thought to be diminished due to the electron-withdrawing nature of the sulfonyl group. Therefore, the stable *syn* intermediate would dominate the reaction pathway to

Table 1 Crystallographic data for pyrroles fused with bicycloalkenes

Compound	**2**	**4**	**5**	*anti*-**10**	**14**	**15**	**19**	*syn*-**23**
Formula	$C_{13}H_{15}NO_2$	$C_{13}H_{16}INO_2$	$C_{19}H_{21}NO_2$	$C_{18}H_{20}N_2O_4$	$C_{12}H_{13}NO_2$	$C_{19}H_{21}N_3O_6$	$C_{12}H_{15}NO_2$	$C_{17}H_{18}N_2O_4$
Formula weight	217.27	345.18	295.39	328.37	203.24	387.40	205.26	314.34
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	P-1	$C2/c$	$C2/c$	$P2_1/n$	P-1	$P2_1/n$
a/Å	8.389(2)	10.366(1)	8.563(2)	10.154(3)	22.057(2)	10.060(2)	9.557(2)	5.612(2)
b/Å	6.518(2)	13.730(2)	15.285(4)	13.488(5)	6.451(2)	19.282(3)	9.576(3)	17.640(2)
c/Å	20.846(2)	9.686(1)	6.317(4)	12.354(7)	18.070(2)	10.397(2)	6.945(2)	16.329(2)
α(°)	90	90.01(1)	100.97(3)	90	90	90	103.60(2)	90
β(°)	90.71(1)	89.97(9)	93.04(3)	97.39(4)	123.980(5)	114.62(1)	107.95(2)	94.40(2)
γ(°)	90	89.943(9)	97.72(2)	90	90	90	105.87(2)	90
V/Å^3	1139.7(3)	1378.7(3)	801.7(6)	1677(1)	2132.2(7)	1833.3(5)	545.0(3)	1611.8(6)
Z	4	4	2	4	8	4	2	4
μ/cm^{-1}	0.85	22.87	0.74	0.93	0.87	1.06	0.85	0.93
Unique refln.	2837	6682	3919	2006	2439	4380	2495	3707
No. obs.[a]	1653[b]	4683	2355	930	1732	2736	1860	1705
R_{int}	0.018	0.021	0.024	0.031	0.020	0.031	0.012	0.042
No. var.	150	316	284	139[c]	169	318	197	241
$R1$[d]	0.070	0.039	0.055	0.064	0.047	0.057	0.039	0.043
R[e]	0.079[f]	0.075	0.051	0.074	0.057	0.084	0.056	0.087
$wR2$[g]	0.252[f]	0.110	0.146	0.100	0.134	0.166	0.118	0.140

[a] $I > 2\sigma(I)$. [b] $I > \sigma(I)$. [c] The methyl group of the ethyl ester moiety is disordered. The ethyl group is treated as an isopropyl group and occupation of the methyl groups is calculated. [d] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2\sigma(I)$ data. [e] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$ for all data. [f] For $I > \sigma(I)$ data. [g] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.



Scheme 7 *Reagents and conditions*: i) PhSCl, CH_2Cl_2, −78 °C; ii) MCPBA, CH_2Cl_2, rt; iii) $CNCH_2CO_2Et$, KOBu^t, THF, rt.

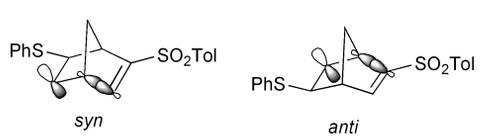


Fig. 1

the observed *syn* isomer **24**. The adduct **24** was converted into sulfone **25** with MCPBA and then to the *syn* benzodipyrrole *syn*-**23** in 71% yield.

X-Ray analysis‡

Single crystals of some pyrroles synthesized above were obtained by slow evaporation of solvents. We carried out X-ray analyses of the pyrroles in order to rationalize their selectivity and reactivity, and the crystallographic data are summarized in Table 1. The most distinctive feature of these pyrroles in crystals is the dimeric structure of pyrrole-2-carboxylate moieties linked by two hydrogen bonds between the pyrrolic protons and the carbonyl oxygen atoms except for **14**. In the crystal of **14**, a polymeric linkage was observed. In all cases, no solvent was included in the crystals.

In all cases, distinctive bond elongation of the pyrrolic C^β–C^β bonds was not observed, probably due to the fact that the double bonds in the pyrrole rings are already localized. Structural features of these pyrroles appeared in the bond angles. Dihedral angles of mean planes of the pyrrole and bicyclic rings and selected valence-bond angles are listed in Table 2. Dihedral angles α of bicyclo[2.2.2]octadiene-fused pyrroles **2** and *anti*-**10** were widened by 1.6° and 2.8° from 120°, respectively, while those of bicyclo[2.2.1]heptadiene-fused pyrroles **14**, **19** and *syn*-**23** were narrowed by 7.1°, 8.15° and 6.9°, respectively. Pyramidalization of the β-pyrrolic sp^2 carbons was observed in all cases: The pyrrole rings are bent in the *exo* direction by 0.7° and 2.7° in the bicyclo[2.2.2]octadiene-fused pyrroles **2** and *anti*-**10**, respectively. On the other hand, in the norbornadiene- and norbornene-fused pyrroles **14**, **19** and *syn*-**23**, the pyrrole rings incline to *endo* by 2.6–4.5°. These phenomena are well in accord with those observed and calculated data for various bicycloalkenes.[22]

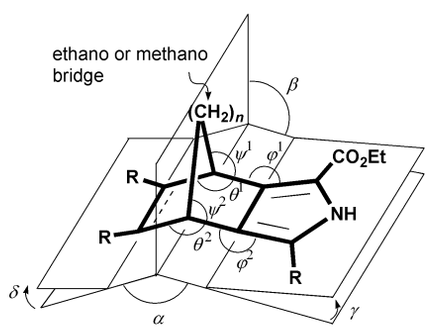


Fig. 2

Thermal analysis of pyrroles fused with a bicyclo[2.2.2]octadiene framework

Thermal behaviour of **2**, *anti*-**9**, *syn*-**10** and *anti*-**10** was examined by differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses. Measurements were performed over the temperature range 100–350 °C. The DSC charts and the calorimetric results are shown in Fig. 3 and Table 3. In the

‡ CCDC reference number 207/487. See http://www.rsc.org/suppdata/p1/b0/b006584f/ for crystallographic files in .cif format.

Table 2 Selected angles (see Fig. 2)

Compound	Dihedral angle (°)				Averaged valence angle (°)		
	α	β	γ	δ	θ^a	Ψ^b	φ^c
2	121.6(3)	119.6(3)	0.7(2)	[d]	106.3	106.0	138.6
4	121.5(3)	119.5(3)	2.5(2)	[d]	106.8[e]		138.2
	121.6(3)	119.5(3)	2.6(2)	[d]	106.6[e]		138.0
5	121.1(1)	120.6(1)	−0.8(1)	[d]	107.0[e]		137.9
anti-**10**	122.8(2)	118.6(2)	2.7(1)[f]		105.9	104.9[g]	137.5
14	112.9(1)	122.02(8)	−3.4(1)	−4(2)	105.3	97.9	145.3
19	111.85(9)	125.61(6)	−4.50(7)	[d]	106.1	99.2	144.8
syn-**23**	113.1(1)	123.56(9)	2.6(1)	−2.5(1)	105.2	97.4[g]	144.3

[a] $(\theta^1 + \theta^2)/2$. [b] $(\Psi^1 + \Psi^2)/2$. [c] $(\varphi^1 + \varphi^2)/2$. [d] Not refined. [e] $(\theta^1 + \theta^2 + \varphi^1 + \varphi^2)/4$. [f] $\gamma = \delta$. [g] Averaged value of four Ψs.

Table 3 Calorimetric results[a]

Compound	Phase transition (melting)				Decomposition			
	T_1 (°C)	T_2 (°C)	T_3 (°C)	ΔH (kJ mol^{-1})	T_1 (°C)	T_2 (°C)	T_3 (°C)	ΔH (kJ mol^{-1})
2	127.0	128.6	130.6	45.4	152.9	220.6	239.6	64.1[b]
anti-**9**	177.0	180.1	186.1	29.8	196.5	237.5	260.0	20.4
					264.8	285.0	298.8	2.6
syn-**10**	159.4	166.1	169.6	18.2	239.8	306.3	322.5	25.7[b]
anti-**10**	268.1	273.1	275.4	[c]	243.1	308.5	318.4	[c]

[a] DSC measurements were performed under the following conditions: scan rate, 10 °C min^{-1}; sampling period, 1 s; scan range, 100–350 °C. T_1, T_2 and T_3 denote temperatures of start, top and end of a peak, respectively. [b] The value was calculated by using the relative molecular mass of the starting material. [c] The two peaks overlapped, and the ΔH-values were not calculated.

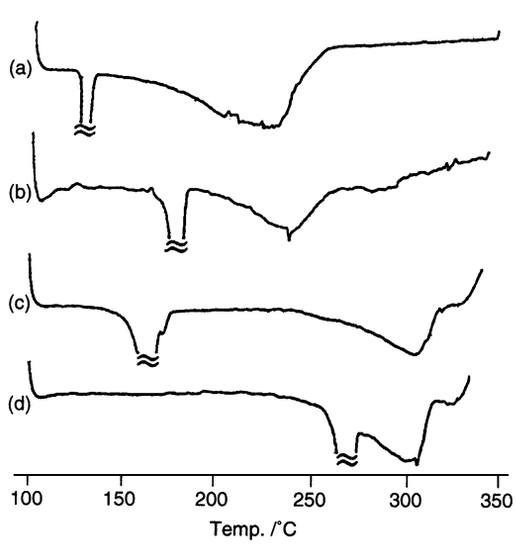
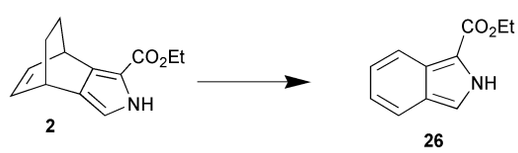


Fig. 3 DSC curves (a): **2**; (b): *anti*-**9**; (c): *syn*-**10**; (d): *anti*-**10**.

cases of **2** and *syn*-**10**, sharp endothermic peaks corresponding to phase transition (mp) and broad endothermic peaks of decomposition were observed in the heating process, while these two peaks overlapped in the case of *anti*-**10**, and two broad endothermic decomposition peaks were observed in the case of *anti*-**9**. The decomposition peaks started at ≈153 °C for **2**, 197 and 265 °C for *anti*-**9**, 240 °C for *syn*-**10** and 243 °C for *anti*-**10**. Although no compound was identified in the proton NMR spectra of any of these samples after the experiments, the decomposition peaks of **2** and *anti*-**9** must correspond to loss of ethylene in the retro-Diels–Alder fashion.

Next, we carried out TG experiments in order to elucidate the decomposition process. In the decomposition of *anti*-**9**, 8% and 28% of weight was lost after the first and second decomposition peaks, respectively. The first peak corresponded to loss of an ethylene molecule and the second corresponded to loss of ethylene and carbon dioxide molecules. In the case of **2**, all the sample disappeared after the second peak. This means the peak involves evaporation of **2** or the decomposed material and this is the reason for the extremely high ΔH-value during the decomposition compared with others. In order to confirm that this peak involved the extrusion of an ethylene molecule in retro-Diels–Alder fashion, we decided to identify the decomposition product of **2** [equation (3)]. Diphenyl ether was chosen as a decomposition medium because of its bp (259 °C) and the pyrrole **2** was refluxed under argon. From TLC monitoring of the reaction, a brightly fluorescent spot appeared at R_f 0.55 ($CHCl_3$). To avoid further decomposition of this material, we stopped the pyrrolysis for 1 h, even though most of the starting material **2** remained. Chromatography on silica gel afforded the isoindole **26** which was contaminated with phthalimide in ≈15% yield. 2*H*-Isoindoles bearing an electron-withdrawing group at the 1- and/or 3-position are known to be fairly stable toward aerial oxidation.[23] As extrusion of the ester moiety from the isoindole *anti*-**9** started at around 265 °C, formation of 2*H*-isoindole from **26** would be possible. Therefore, phthalimide must be formed by the oxidation of **26** with trace oxygen present in the reaction medium or by the oxidation of 2*H*-isoindole during the work-up manipulation. We concluded that extrusion of ethylene from **2** took place to form **26** and then **26** evaporated or decomposed to 2*H*-isoindole, which simultaneously evaporated, in the decomposition peak of **2**.



(3)

The decomposition of **10** was determined to involve the loss of ethyl ester moieties by TG analysis: over 52% loss of weight corresponding to the extrusion of three molecules of ethylene

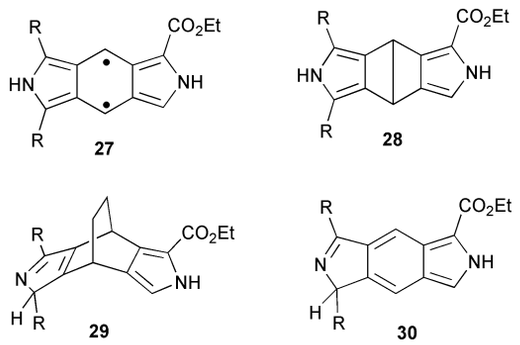


Fig. 4

and two molecules of carbon dioxide was observed during the decomposition. There are two possible routes in the extrusion of ethylene from the bicyclooctadiene skeleton of **10**. Extrusion of ethylene from the bridging ethano moiety of **10** would give an unfavourable diradical or Dewar structure **27** or **28**, which then would isomerize to a novel heterocyclic ring system, 1,6-dihydrobenzo[1,2-*c*:4,5-*c*′]dipyrrole **30** (Fig. 4). Tautomerism between pyrrole and pyrrolenine in **10** would give **29**, which would then undergo decomposition under pyrolytic conditions to give **30**. However, the energy cost of the transformation from pyrrole to pyrrolenine is over 70 kJ mol^{-1}.[24] Both the possible decomposition routes in the loss of ethylene involve high-energy-costing steps. This would be one of the reasons for the apparent lack of formation of identifiable products in the pyrrolysis of **10**.

Conclusions

We have achieved the synthesis of various pyrroles fused with rigid bicyclo[2.2.2]- and bicyclo[2.2.1]alkenes at the β-positions starting from Diels–Alder adducts of cyclohexadiene and cyclopentadiene with 2-nitro-1-(phenylsulfonyl)ethylene, 1,2-bis(phenylsulfonyl)ethylene and tosylacetylene. These pyrroles would be promising precursors for preparations of novel materials such as porphyrin arrays, organic conductive materials, and fluorescent dyes, which have largely extended or loosely interacting π-systems. Studies along this line are underway in our laboratories.

Experimental

General

Mps were measured on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were obtained with a JEOL GSX-270 or EX-400 spectrometer at ambient temperature by using $CDCl_3$ as solvent, and tetramethylsilane as internal standard for ^1H and ^{13}C. Coupling constants (*J*-values) are given in Hz. Mass spectra were measured with a Hitachi M80B spectrometer under EI (electron impact, 20 eV) conditions. DSC and TG experiments were performed on a Seiko Instruments EXSTAR 6000 apparatus. All X-ray measurements were made at 25 °C on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation and a 12 kW rotating-anode generator. THF and ether were distilled from sodium benzophenone ketyl, and dichloromethane was distilled from CaH_2 prior to use. DMF was distilled under reduced pressure and then stored over molecular sieves (MS) 4 Å. Pyridine, hexane and diphenyl ether were distilled from CaH_2 and stored over MS 4 Å. Acetonitrile was distilled from P_2O_5 and then from CaH_2, and stored over MS 4 Å. Potassium *tert*-butoxide was sublimed at 200 °C under reduced pressure (≈0.1 mmHg) and then dissolved in dry THF (1.0 mol L^{-1}). Ethyl isocyanoacetate was prepared according to the literature procedure.[25] Benzenesulfenyl chloride[26] was prepared from thiophenol and sulfuryl dichloride in hexane in the presence of a catalytic amount of triethylamine, distilled under reduced pressure (50 °C/4 mmHg), and stored under nitrogen in a refrigerator. Other commercially available materials were used without further purification.

General procedures

DBU method for pyrrole formation. To a stirred solution of a nitro compound and ethyl isocyanoacetate (1.1 equiv.) in dry THF or dry MeCN (0.07 mol L^{-1}) was added DBU (2.2 equiv.) by syringe at room temperature under argon. After disappearance of the starting nitro compound had been checked by TLC (8–12 h), the reaction was quenched by adding 5% aq. HCl. The mixture was extracted three times with chloroform or ethyl acetate. The organic extract was washed successively with saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed on silica gel.

Potassium *tert*-butoxide method for pyrrole formation. Ethyl isocyanoacetate (1.2 equiv.) was added to a 1.0 M solution of potassium *tert*-butoxide in THF (1.4 equiv.) by a syringe at 0 °C under argon. To the stirred suspension of an anion of isocyanoacetate was added a solution of a sulfone in dry THF (0.1 mol L^{-1}) at the same temperature, and then the mixture was stirred at room temperature. After disappearance of the starting sulfone had been checked by TLC (within 2 h in most cases), the reaction was quenched by adding 5% aq. HCl. The mixture was extracted three times with chloroform or ethyl acetate. The organic extract was washed successively with saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed on silica gel.

Addition of benzenesulfenyl chloride. To a stirred solution of an olefin in dry dichloromethane (0.1 mol L^{-1}) was added benzenesulfenyl chloride (1.0 equiv.) by syringe at −78 °C under argon, and then the mixture was warmed to room temperature. After disappearance of the starting olefin had been checked by TLC (within 4 h in most cases), the solvent was removed *in vacuo*. The residual material was purified by recrystallization or chromatography on silica gel.

Oxidation of sulfide to sulfone. To a stirred solution of sulfide in dry dichloromethane or chloroform (0.1 mol L^{-1}) was added MCPBA (2.4 equiv.) at 0 °C. After the mixture had been stirred for 2 h at room temperature, aq. $NaHSO_3$ was added. The mixture was extracted three times with ethyl acetate. The organic extract was washed successively with aq. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residual material was purified by recrystallization or chromatography on silica gel.

Elimination of HCl from β-chloro sulfone. To a solution of a β-chloro sulfone in dry pyridine or dichloromethane (0.5 mol L^{-1}) was added DBU (1.2 equiv.) by syringe at room temperature. After 30 min, 2% aq. HCl was added and then the mixture was extracted with ethyl acetate. The organic extract was washed successively with water, saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residual material was purified by recrystallization or chromatography on silica gel.

Hydrogenation. Palladium on charcoal (10% w/w) in THF was activated three times by evacuation followed by filling with hydrogen. To the activated suspension of Pd/C was added a solution of a compound in THF under one atmospheric pressure of hydrogen and the mixture was rigorously stirred overnight. After the catalyst had been removed by filtration through Celite, the solvent was removed *in vacuo*. The residual material was purified by recrystallization or chromatography on silica gel.

(1*S,2*R**,3*R**,4*R**,5*R**,6*R**)-2-Chloro-5-nitro-6-(phenylsulfonyl)-3-phenylthiobicyclo[2.2.2]octane (*endo*-7) and (1*S**,2*R**,3*R**,4*R**,5*R**,6*R**)-2-chloro-6-nitro-5-phenylsulfonyl-3-(phenylthio)bicyclo[2.2.2]octane (*exo*-7)**

The reaction of **1** (*endo*/*exo* = 3/2; 0.206 g, 0.71 mmol) with benzenesulfenyl chloride (0.71 mmol) followed by recrystallization from diethyl ether–hexane gave 0.258 g (83%) of the title compounds (*endo*/*exo* = 3/2) as colourless crystals, mp 153–154 °C (*endo* : *exo* = 3 : 2) (Found: C, 54.82; H, 4.55; N, 3.22. $C_{20}H_{20}ClO_4S_2$ requires C, 54.85; H, 4.60; N, 3.20%); R_f 0.55 (30% EtOAc–hexane); δ_H *endo*-**7** 1.61 (1H, m, H^7), 1.69 (1H, m, H^8), 2.22 (1H, m, H^8), 2.41 (1H, m, H^7), 2.60 (1H, m, H^4), 2.66 (1H, m, H^1), 3.33 (1H, dt, *J* 5.9 and 2.0, H^3), 3.89 (1H, m, H^2), 4.66 (1H, dt, *J* 7.3 and 1.7, H^6), 5.15 (1H, dd, *J* 7.3 and 2.4, H^5), 7.2–7.75 (8H, m, ArH) and 7.90 (2H, m, ArH); *exo*-**7** 1.41 (1H, m, 2 × H^8), 1.63 (2H, m, 2 × H^7), 2.20 (1H, m, H^8), 2.30 (1H, m, H^4), 2.74 (1H, m, H^1), 3.89 (1H, m, H^2), 4.17 (1H, dd, *J* 8.0 and 1.3, H^5), 4.33 (1H, dt, *J* 6.8 and 2.0, H^3), 5.59 (1H, dd, *J* 7.8 and 1.5, H^6), 7.2–7.75 (8H, m, ArH) and 7.90 (2H, m, ArH); δ_C (Signals could not be assigned for the isomers and the DEPT results are shown in the parentheses) 17.5 (t), 18.9 (t), 19.2 (t), 19.6 (t), 31.6 (d), 36.0 (d), 37.9 (d), 42.6 (d), 51.3 (d), 51.6 (d), 58.3 (d), 60.7 (d), 62.3 (d), 63.3 (d), 78.4 (d), 83.0 (d), 128.1 (d), 128.3 (d), 128.4 (d), 128.4 (d), 129.3 (d), 129.4 (d), 129.6 (d), 129.7 (d), 131.8 (d), 132.3 (s), 132.7 (s), 132.9 (d), 134.5 (d), 134.7 (d), 136.7 (s) and 137.4 (s); ν_{max} (KBr)/cm^{-1} 1560, 1550, 1371, 1317, 1305, 1149 and 754; *m*/*z* (%) 439 [M^+(^{37}Cl), 2], 437 [M^+(^{35}Cl), 6], 401 (20), 355 (100), 260 (35), 186 (41) and 170 (44).

(1*S,2*R**,3*R**,4*R**,5*R**,6*R**)-2-Chloro-5-nitro-3,6-bis(phenylsulfonyl)bicyclo[2.2.2]octane (*endo*-8) and (1*S**,2*R**,3*R**,4*R**,5*R**,6*R**)-2-chloro-6-nitro-3,5-bis(phenylsulfonyl)bicyclo-[2.2.2]octane (*exo*-8)**

The oxidation of **7** (*endo*/*exo* = 3/2; 0.191 g, 0.436 mmol) according to the general procedure followed by recrystallization from CH_2Cl_2–diethyl ether–hexane gave 0.193 g (94%) of the title compounds (*endo*/*exo* = 3/2) as colourless crystals, mp 210–212 °C (Found: C, 51.02; H, 4.32; N, 2.95. $C_{20}H_{20}ClNO_6S_2$ requires C, 51.12; H, 4.29; N, 2.96%); R_f 0.45 (40% EtOAc–hexane); δ_H *endo*-**8** 1.64 (1H, m, H^7), 1.75 (1H, m, H^8), 2.3–2.5 (2H, m, H^7 and H^8), 2.77 (1H, m, H^4), 3.22 (1H, d, *J* 5.9, H^3), 3.32 (1H, m, H^1), 4.53 (2H, m, H^2 and H^6), 5.13 (1H, dd, *J* 6.8 and 2.9, H^5) and 7.5–8.0 (10H, m, ArH); *exo*-**8** 1.47 (1H, m, H^8), 1.7–1.9 (2H, m, 2 × H^7), 2.22 (1H, m, H^8), 2.85 (1H, m, H^4), 3.07 (1H, m, H^1), 5.17 (1H, dd, *J* 7.5 and 1.7, H^5), 4.42 (1H, dt, *J* 6.7 and 1.5, H^3), 4.17 (1H, dd, *J* 6.7 and 2.6, H^2), 5.48 (1H, d, *J* 7.5, H^6), 7.2–7.75 (8H, m, ArH) and 7.90 (2H, m, ArH); δ_C 18.4 (*endo*), 18.8 (*exo*), 19.4 (*endo*), 20.0 (*exo*), 27.6 (*exo*), 33.5 (*endo*), 35.9 (*endo*), 42.5 (*exo*), 53.8 (*exo*), 55.1 (*endo*), 58.5 (*endo*), 63.3 (*exo*), 65.8 (*exo*), 66.5 (*endo*), 78.2 (*exo*), 83.0 (*endo*), 128.3, 128.5, 128.6, 128.7, 129.6, 129.6, 129.8, 129.9, 134.5, 134.7, 134.9, 135.0, 136.5, 137.2, 137.9 and 138.3; ν_{max} (KBr)/cm^{-1} 1558, 1323, 1298, 1151, 725 and 609; *m*/*z* (%) 469 [M^+(^{35}Cl), 1], 434 (28), 328 (21), 281 (30), 186 (68), 141 (61) and 125 (100).

Ethyl 6-phenylsulfonyl-4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (*syn*-9) and ethyl 5-phenylsulfonyl-4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (*anti*-9)

The reaction of **8** (*endo*/*exo* = 3/2; 0.174 g, 0.371 mmol) with ethyl isocyanoacetate (0.096 mL, 0.88 mmol) was carried out according to the general procedure. Chromatographic purification gave 0.050 g (41%) of **9** as a mixture of isomers (*anti*/*syn* = 3/2). Separation of the isomers was performed by preparative gel permeation chromatography and recrystallization.

The title compounds (*syn*/*anti* = 3/4; 0.642 g, 94%) were also prepared by dehydrochlorination of **12** (*syn*/*anti* = 3/4; 0.755 g, 1.92 mmol) according to the general procedure. *syn*-**9**: colourless crystals, mp 52–54 °C; R_f 0.4 (40% EtOAc–hexane); δ_H 1.29 (3H, t, *J* 7.0), 1.57 (2H, m), 1.63 (2H, m), 4.13 (1H, m, H^4), 4.05–4.25 (2H, m), 4.66 (1H, m, H^7), 6.57 (1H, d, *J* 2.5, H^3), 7.44 (2H, m, ArH), 7.54 (2H, m, ArH and H^5), 7.79 (2H, m, ArH) and 8.47 (1H, br s, NH); δ_C 14.4, 26.7, 26.9, 34.6 (2C), 60.1, 113.6, 114.5, 127.6, 128.7, 128.9, 133.0, 133.3, 140.0, 146.3, 147.9 and 161.1; ν_{max} ($CHCl_3$)/cm^{-1} 3452, 1691, 1602, 1315, 1302 and 1151. *anti*-**9** colourless crystals, mp 236–238 °C (Found: C, 63.44; H, 5.33; N, 3.83. $C_{19}H_{19}NO_4S$ requires C, 63.85; H, 5.36; N, 3.92%); R_f 0.45 (40% EtOAc–hexane); δ_H 1.37 (3H, t, *J* 7.0), 1.47 (2H, m), 1.61 (2H, m), 4.19 (1H, m, H^4), 4.31 (2H, m), 4.61 (1H, m, H^7), 6.44 (1H, d, *J* 2.4, H^3), 7.49 (3H, m, 2 × ArH and H^6), 7.58 (1H, m, ArH), 7.82 (2H, m, ArH) and 8.51 (1H, br s, NH); δ_C 14.5, 26.1, 27.6, 34.0, 34.9, 60.2, 113.2, 114.8, 127.3, 128.9, 129.1, 133.1, 133.5, 139.8, 145.5, 148.5 and 161.1; ν_{max} (KBr)/cm^{-1} 3307, 1689, 1323, 1299, 1292, 1155, 1145, 730 and 579; *m*/*z* (%) 329 (M^+, 100), 283 (24), 216 (9) and 158 (11).

Diethyl 2,4,6,8-tetrahydro-4,8-ethanobenzo[1,2-*c*:4,5-*c*′]dipyrrole-1,7-dicarboxylate (*syn*-10)

The title compound (194 mg, 81%) was prepared from *anti*-**9** (261 mg, 0.73 mmol) according to the potassium *tert*-butoxide procedure. *syn*-**10**: colourless crystals, mp 168–170 °C; R_f 0.45 (40% EtOAc–hexane); δ_H 1.40 (6H, t, *J* 7.0), 1.68 (2H, m), 1.74 (2H, m), 4.24 (1H, m, H^4), 4.34 (4H, q, *J* 7.0), 5.28 (1H, m, H^8), 6.62 (2H, d, *J* 2.9, H^3 and H^5) and 8.77 (2H, br s, NH); δ_C 14.8, 28.4, 29.7, 31.1, 31.8, 60.2, 113.7, 115.3, 132.0, 135.8 and 162.2; ν_{max} (KBr)/cm^{-1} 3319, 1674, 1419, 1321, 1271, 1147, 1093 and 1045; *m*/*z* (%) 328 (M^+, 0.9), 300 (98), 254 (100), 208 (41) and 180 (5).

Diethyl 2,4,6,8-tetrahydro-4,8-ethanobenzo[1,2-*c*:4,5-*c*′]dipyrrole-1,5-dicarboxylate (*anti*-10)

The title compound (84 mg, 78%) was prepared from *syn*-**9** (118 mg, 0.33 mmol) according to the potassium *tert*-butoxide procedure. *anti*-**10**: colourless crystals, mp 264–266 °C (decomp.) (Found: C, 65.68; H, 6.25; N, 8.32. $C_{18}H_{20}N_2O_4$ requires C, 65.84; H, 6.14; N, 8.53%); R_f 0.5 (40% EtOAc–hexane); δ_H 1.38 (6H, t, *J* 7.3), 1.72 (4H, m), 4.32 (4H, m), 4.77 (2H, m, H^4 and H^8), 6.68 (2H, d, *J* 1.5, H^3 and H^7) and 8.47 (2H, br s, NH); δ_C 14.5, 28.7, 31.1, 59.9, 113.9, 114.4, 130.9, 136.7 and 161.6; ν_{max} (KBr)/cm^{-1} 3307, 1670, 1419, 1325, 1298, 1149 and 1034; *m*/*z* (%) 328 (M^+, 1.3), 300 (98), 254 (100), 208 (37) and 181 (6).

Ethyl (4*R,5*R**,6*R**,7*S**)-5-chloro-6-phenylthio-4,5,6,7-tetrahydro-4,7-ethano-2*H*-isoindole-1-carboxylate (*syn*-11) and ethyl (4*R**,5*S**,6*S**,7*S**)-6-chloro-5-phenylthio-4,5,6,7-tetrahydro-4,7-ethano-2*H*-isoindole-1-carboxylate (*anti*-11)**

The reaction of **2** (0.765 g, 3.52 mmol) with benzenesulfenyl chloride (0.509 g, 0.415 mL, 3.52 mmol) followed by trituration with diethyl ether–hexane gave 1.261 g (99%) of an isomeric mixture (*syn*:*anti* = 3 : 4) of the title compounds. The *anti*-isomer could be isolated by a combination of chromatography on silica gel (20% EtOAc–hexane) and recrystallization from CH_2Cl_2–diethyl ether–hexane. *anti*-**11**: colourless crystals, mp 110–111 °C (Found: C, 62.94; H, 5.57; N, 3.86. $C_{19}H_{20}ClNO_2S$ requires: C, 63.06; H, 5.57; N, 3.87%); R_f 0.55 (30% EtOAc–hexane); δ_H 1.34 (3H, t, *J* 7.3), 1.35 (1H, m), 1.50 (1H, m), 1.89 (1H, m), 2.34 (1H, m), 3.13 (1H, m), 3.56 (1H, m), 3.75 (1H, m), 3.84 (1H, m), 4.32 (2H, m), 6.76 (1H, d, *J* 2.4, H^3), 7.2–7.3 (3H, m, ArH), 7.44 (2H, m, ArH) and 9.39 (1H, br s, NH); δ_C 14.5, 19.5, 27.0, 34.1, 36.8, 58.2, 60.2, 65.2, 115.8, 116.4, 124.7, 127.1, 129.0, 130.3, 131.8, 134.7 and 161.3; ν_{max} (KBr)/cm^{-1} 3305, 1676, 1431, 1317, 1292, 1149, and 594; *m*/*z* (%) 363 [M^+(^{37}Cl), 5], 361 [M^+(^{35}Cl), 13], 252 (13), 216 (37) and 190

(100). *syn*-**11** R_f 0.5 (30% EtOAc–hexane); δ_H 1.21 (3H, t, *J* 7.3), 1.36 (1H, m), 1.53 (1H, m), 1.82 (1H, m), 2.32 (1H, m), 3.22 (1H, m), 3.56 (1H, m), 3.69 (1H, m), 3.75 (1H, m), 4.2–4.4 (2H, m), 6.72 (1H, d, *J* 2.4, H^3), 7.2–7.3 (3H, m, ArH), 7.47 (2H, m, ArH) and 9.39 (1H, br s, NH); δ_C 14.2, 18.9, 26.4, 34.0, 36.6, 58.2, 60.0, 65.1, 115.0, 117.6, 125.4, 127.1, 128.8, 129.7, 132.0, 134.6 and 161.7.

Ethyl (4*R**,5*R**,6*R**,7*S**)-5-chloro-6-phenylsulfonyl-4,5,6,7-tetrahydro-4,7-ethano-2*H*-isoindole-1-carboxylate (*syn*-12) and ethyl (4*R**,5*S**,6*S**,7*S**)-6-chloro-5-phenylsulfonyl-4,5,6,7-tetrahydro-4,7-ethano-2*H*-isoindole-1-carboxylate (*anti*-12)

The oxidation of **2** (0.745 g, 2.06 mmol) followed by trituration with diethyl ether–hexane gave 0.755 g (93%) of an isomeric mixture (*syn*:*anti* = 3:4) of the title compounds. The pure *anti*-isomer was obtained by the oxidation of *anti*-**11**. *anti*-**12**: colourless crystals, mp 180–181 °C (Found: C, 57.65; H, 4.98; N, 3.44. $C_{19}H_{20}ClNO_4S$ requires C, 57.94; H, 5.12; N, 3.56%); R_f 0.25 (30% EtOAc–hexane); δ_H 1.36 (3H, t, *J* 7.0), 1.41 (1H, m), 1.52 (1H, m), 1.90 (1H, m), 2.28 (1H, m), 3.48 (1H, m), 3.78 (1H, m), 3.81 (1H, m), 4.19 (1H, m), 4.33 (2H, m), 6.73 (1H, d, *J* 2.4, H^3), 7.54 (2H, m, ArH), 7.65 (1H, m, ArH), 7.82 (2H, m, ArH) and 8.93 (1H, br s, NH); δ_C 14.5, 18.6, 27.8, 28.4, 36.8, 57.0, 60.2, 73.2, 115.6, 115.9, 123.2, 128.7, 129.2, 129.4, 133.9, 138.5 and 161.1; ν_{max} (KBr)/cm^{-1} 3307, 1609, 1429, 1330, 1105, 740 and 690; *m*/*z* (%) 395 [M^+(^{37}Cl), 6], 393 [M^+(^{35}Cl), 20], 348 (3), 254 (26), 252 (100), 206 (36) and 190 (62). *syn*-**12** R_f 0.25 (30% EtOAc–hexane); δ_H 1.41 (3H, t, *J* 7.0), 1.3–1.6 (2H, m), 1.90 (1H, m), 2.28 (1H, m), 3.29 (1H, m), 3.53 (1H, m), 4.13 (1H, m), 4.24 (1H, m), 4.35 (2H, m), 6.67 (1H, d, *J* 2.9, H^3), 7.51 (2H, m, ArH), 7.63 (1H, m, ArH), 7.86 (2H, m, ArH) and 9.30 (1H, br s, NH); δ_C 14.4, 19.2, 27.1, 28.9, 36.6, 56.9, 60.0, 73.0, 115.0, 116.6, 124.2, 128.9, 129.1, 130.2, 133.7, 137.9 and 161.7.

Ethyl 4,5,6,7-tetrahydro-4,7-methano-2*H*-isoindole-1-carboxylate 19

The title compound was obtained in 95% yield from **18** (4.05 g, 15 mmol) according to the modified general procedure using 2.4 equiv. of potassium *tert*-butoxide. **19**: colourless crystals, mp 114–116 °C (Found: C, 70.10; H, 7.50; N, 6.75. $C_{12}H_{15}NO_2$ requires C, 70.22; H, 7.37; N, 6.82%); R_f 0.55 ($CHCl_3$); δ_H 1.17 (2H, m), 1.35 (3H, t, *J* 7.3), 1.63 (1H, m), 1.87 (3H, m), 3.28 (1H, m, H^4), 3.58 (1H, m, H^7), 4.31 (2H, m), 6.52 (1H, d, *J* 2.4, H^3) and 8.51 (1H, br s, NH); δ_C 14.5, 28.0, 28.7, 38.4, 39.3, 51.9, 59.8, 112.2, 113.1, 135.3, 141.0 and 161.7; ν_{max} (KBr)/cm^{-1} 3305, 1685, 1415, 1323, 1138 and 1107; *m*/*z* (%) 205 (M^+, 99), 190 (13), 177 (100), 159 (65), 132 (49), 131 (70) and 104 (100).

(1*S**,2*R**,3*R**,4*R**,5*R**,6*R**)-2-Chloro-5-nitro-6-phenylsulfonyl-3-(phenylthio)bicyclo[2.2.1]heptane (*endo*-20) and (1*S**,2*R**, 3*R**,4*R**,5*R**,6*R**)-2-chloro-6-nitro-5-phenylsulfonyl-3-(phenylthio)bicyclo[2.2.1]heptane (*exo*-20)

The reaction of **13** (*endo*/*exo* = 2/1; 1.754 g, 6.30 mmol) was carried out according to the general procedure. After 48 h, the reaction mixture was concentrated and the residue was recrystallized from CH_2Cl_2–diethyl ether–hexane to give 1.409 g (53%) of pure *endo*-**20**. The reaction of **13** (*endo*/*exo* = 2/1; 0.558 g, 2.0 mmol) was carried out according to the general procedure. After 14 days, the reaction mixture was concentrated and the residue was chromatographed on silica gel (20% EtOAc–hexane) to give 0.620 g (73%) of **20** as a mixture of isomers (*endo*/*exo* = 5/2). Isolation of *exo*-**20** was not attempted. *endo*-**20**: colourless crystals, mp 128–129 °C (Found: C, 53.59; H, 4.28; N, 3.40. $C_{19}H_{18}ClNO_2S_2$ requires C, 53.83; H, 4.28; N, 3.30%); R_f 0.2 (20% EtOAc–hexane); δ_H 2.10 (1H, m, H^7), 2.32 (1H, m, H^7), 3.01 (1H, dd, *J* 4.4 and 2.9, H^3), 3.04 (1H, m, H^1), 3.07 (1H, m, H^4), 4.08 (1H, t, *J* 4.4, H^2), 4.65 (1H, dd, *J* 5.4 and 2.4, H^6), 5.29 (1H, dd, *J* 5.4 and 4.9, H^5), 7.32 (5H, m, ArH), 7.62 (2H, m, ArH), 7.73 (1H, m, ArH) and 7.94 (2H, m, ArH); δ_C 34.1, 47.1, 48.7, 51.8, 61.4, 63.0, 85.5, 128.0, 128.4, 129.4, 129.8, 131.3, 132.7, 134.7 and 137.2; ν_{max} (KBr)/cm^{-1} 1547, 1306, 1153, 740, 687 and 580; *m*/*z* (%) 425 [M^+(^{37}Cl), 5], 423 [M^+(^{35}Cl), 15], 341 (12), 246 (77), 187 (68), 170 (100), 135 (81), 125 (66) and 110 (73). *exo*-**20** δ_H 1.83 (1H, m, H^7), 2.14 (1H, m, H^7), 2.86 (1H, dd, *J* 4.4 and 2.9, H^4), 3.18 (1H, m, H^1), 4.15 (1H, t, *J* 4.4, H^5), 4.27 (1H, dd, *J* 5.0 and 3.7, H^2), 4.38 (1H, dd, *J* 5.0 and 2.9, H^3), 5.29 (1H, dd, *J* 4.4 and 1.5, H^6), 7.2–7.8 (8H, m, ArH) and 7.94 (2H, m, ArH).

(1*S**,2*R**,3*R**,4*R**,5*R**,6*R**)-2-Chloro-5-nitro-3,6-bis(phenylsulfonyl)bicyclo[2.2.1]heptane 21

The oxidation of *endo*-**20** (0.423 g, 1.0 mmol) according to the general procedure followed by chromatographic purification (silica gel; 30% EtOAc–hexane) gave 0.454 g (100%) of **21** as colourless crystals, mp 169–171 °C (Found: C, 49.97; H, 4.30; N, 3.05. $C_{19}H_{18}ClNO_4S_2$ requires C, 50.05; H, 3.98; N, 3.07%); R_f 0.85 (50% EtOAc–hexane); δ_H 2.36 (2H, m, 2 × H^7), 2.90 (1H, m, H^3), 3.11 (1H, m, H^1), 3.50 (1H, m, H^4), 4.47 (1H, m, H^6), 4.65 (1H, m, H^2), 5.29 (1H, m, H^5), 7.61 (4H, m, ArH), 7.73 (2H, m, ArH), 7.86 (2H, m, ArH) and 7.93 (2H, m, ArH); δ_C 34.4, 44.8, 46.9, 56.4, 61.7, 67.9, 85.2, 128.4, 128.5, 129.8, 129.9, 134.8, 134.9, 136.9 and 137.0; ν_{max} (KBr)/cm^{-1} 1554, 1321, 1311, 1155, 1086, 723 and 688; *m*/*z* (%) 420 (M^+ − Cl, 2), 409 (M^+ − NO_2, 1), 368 (2), 314 (18), 203 (58), 141 (75) and 125 (100).

Ethyl (4*R**,5*S**,6*S**,7*S**)-5,6-bis(phenylsulfonyl)-4,5,6,7-tetrahydro-4,7-methano-2*H*-isoindole-1-carboxylate 22

The reaction of **21** (0.456 g, 1.0 mmol) with ethyl isocyanoacetate (2.2 mmol) and DBU (6.6 mmol) was carried out according to the modified procedure at 55 °C. Chromatographic purification (silica gel; 40% EtOAc–hexane) gave 0.070 g (15%) of the title compound as colourless crystals, mp 194–195 °C; R_f 0.4 (50% EtOAc–hexane); δ_H 1.26 (3H, t, *J* 7.0), 2.04 (1H, m, H^8), 2.56 (1H, m, H^8), 3.58 (1H, dd, *J* 4.9 and 2.0, H^6), 3.79 (1H, m, H^7), 3.90 (1H, m, H^4), 4.06 (2H, m), 4.47 (1H, dd, *J* 4.9 and 3.9, H^5), 6.81 (1H, d, *J* 2.4, H^3), 7.4–7.7 (6H, m, ArH), 7.86 (4H, m, ArH) and 8.19 (1H, br s, NH); δ_C 14.3, 42.2, 44.0, 50.5, 60.0, 67.4, 68.2, 113.5, 116.8, 128.4, 128.5, 129.0, 129.3, 129.7, 133.8, 134.0, 135.3, 138.6, 139.8 and 160.7; ν_{max} (KBr)/cm^{-1} 3381, 1703, 1531, 1323, 1302, 1146, 1103, 688 and 577; *m*/*z* (%) 485 (M^+, 13), 344 (100), 298 (57), 202 (50), 177 (17), 174 (17) and 156 (74).

Diethyl 2,4,6,8-tetrahydro-4,8-methanobenzo[1,2-*c*:4,5-*c*′]-dipyrrole-1,7-dicarboxylate (*syn*-23) and diethyl 2,4,6,8-tetrahydro-4,8-methanobenzo[1,2-*c*:4,5-*c*′]dipyrrole-1,5-dicarboxylate (*anti*-23)

The reaction of **25** (see below) (0.211 g, 0.50 mmol) with ethyl isocyanoacetate (1.2 mmol) and potassium *tert*-butoxide (2.1 mmol) was carried out according to the general procedure. Recrystallization (CH_2Cl_2–diethyl ether–hexane) of the reaction mixture gave 0.111 g (71%) of pure *syn*-**23**. Isolation of *anti*-**23** was not attempted. *syn*-**23**: colourless crystals, mp 188–189 °C (Found: C, 64.96; H, 5.91; N, 8.64. $C_{17}H_{18}N_2O_4$ requires C, 64.96; H, 5.77; N, 8.91%); R_f 0.2 ($CHCl_3$); δ_H 1.38 (6H, t, *J* 7.0), 2.78 (2H, m), 4.13 (1H, br s, H^4), 4.2–4.4 (4H, m), 4.68 (1H, br s, H^8), 6.55 (2H, d, *J* 2.4, H^3 and H^5) and 8.16 (2H, br s, NH); δ_C 14.5, 40.1, 41.7, 60.0, 71.1, 112.6, 114.9, 139.0, 142.7 and 161.2; ν_{max} (KBr)/cm^{-1} 3313, 1689, 1664, 1412, 1327, 1134 and 1117; *m*/*z* (%) 314 (M^+, 58), 285 (26), 268 (57), 239 (75), 221 (100), 194 (84) and 140 (52). *anti*-**23** δ_H 1.36 (6H, t, *J* 7.3), 2.78 (2H, m), 4.2–4.4 (4H, m), 4.41 (2H, br s, H^4 and H^8), 6.58 (2H, d, *J* 2.4, H^3 and H^5) and 8.11 (2H, br s, NH).

(1*R,4*R**,5*S**,6*S**)-5-Chloro-6-phenylthio-2-tosylbicyclo[2.2.1]-hept-2-ene 24**

The phenylsulfenylation of **16** (0.765 g, 3.1 mmol) was performed according to the general procedure. Chromatographic purification (silica gel; 20% EtOAc–hexane) gave 1.201 g (100%) of the title compound as colourless crystals, mp 96–98 °C (Found: C, 61.41; H, 4.93. $C_{20}H_{19}ClO_2S_2$ requires C, 61.45; H, 4.99%); R_f 0.75 ($CHCl_3$); δ_H 1.87 (1H, m, H^7), 2.01 (1H, m, H^7), 2.43 (3H, s), 2.83 (1H, m, H^6), 3.10 (1H, m, H^1), 3.40 (1H, m, H^4), 4.18 (1H, m, H^5), 7.02 (1H, m, H^3), 7.2–7.4 (7H, m, ArH) and 7.69 (2H, m, ArH); δ_C 21.6, 46.8, 49.0, 50.7, 55.8, 63.5, 127.1, 128.1, 129.0, 129.9, 130.5, 134.0, 136.0, 144.5, 144.7 and 150.0; ν_{max} (KBr)/cm^{-1} 1308, 1300, 1142, 739, 687, 656 and 586; *m*/*z* (%) 392 [M^+(^{37}Cl), 2], 390 [M^+(^{35}Cl), 5], 355 (59), 172 (71), 170 (100) and 135 (69).

(1*R,4*R**,5*S**,6*S**)-5-Chloro-6-phenylsulfonyl-2-tosylbicyclo-[2.2.1]hept-2-ene 25**

The oxidation of **24** (0.781 g, 2.0 mmol) followed by chromatographic purification on silica gel ($CHCl_3$) gave 0.719 g (85%) of **25** as colourless crystals, mp 160–162 °C (Found: C, 56.75; H, 4.90. $C_{20}H_{19}ClO_4S_2$ requires C, 56.80; H, 4.53%); R_f 0.45 ($CHCl_3$); δ_H 1.85 (1H, m, H^7), 2.30 (1H, m, H^7), 2.48 (3H, s), 2.61 (1H, dd, *J* 4.4 and 2.4, H^6), 3.48 (1H, m, H^1), 3.52 (1H, m, H^4), 4.70 (1H, m, H^5), 7.09 (1H, m, H^3), 7.30 (2H, m, ArH) and 7.55–7.8 (7H, m, ArH); δ_C 21.7, 45.8, 46.4, 50.8, 57.6, 73.0, 128.2, 128.3, 129.5, 130.2, 133.7, 134.3, 136.0, 138.7, 145.0, 146.4 and 150.6; ν_{max} (KBr)/cm^{-1} 1321, 1308, 1147, 604 and 582; *m*/*z* (%) 422 [M^+(^{35}Cl), 2], 296 (2), 281 (3), 220 (88), 155 (12), 139 (100) and 125 (26).

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