Organic & Biomolecular Chemistry

Dynamic Article Links

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 8321

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PAPER

Sulfonamide carbazole receptors for anion recognition†

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Received 8th July 2011, Accepted 14th September 2011
DOI: 10.1039/c1ob06126g

Carbazole-based receptors functionalized with two sulfonamide groups have been synthesized and their properties as anion receptors have been evaluated. The receptor with bis(trifluoromethyl)aniline groups has shown a very high affinity for halide ions, especially remarkable as only two hydrogen bonds are formed in the complexes. ^{1}H NMR and fluorescence titrations have been carried out and binding constants up to 7.9×10^6 M^{-1} have been reached. X-ray structures have been obtained and a modelling study has shown the possible reasons for the large affinity of these compounds for halide anions.

Introduction

The design and synthesis of receptors for anion recognition through hydrogen bonds is an active field in research.[1] Amides,[2] ureas and thioureas,[3] guanidines[4] and sulfonamides,[5] among others, have shown their potential as hydrogen-bond donors and many anion receptors have included them. The directional character of H-bonds makes an effective binding to the anions feasible when a number of H-bond donor groups are properly positioned on a molecular platform. Calixarenes,[6] xanthenes,[7] anthracenes,[8] binaphthyls,[9] chromenones[10] and carbazoles[11] are only a few examples of frameworks that have been used to build molecular clefts for anion recognition.

Since the pioneering work of Jurczak,[12] much attention has been focused on the 1,8-diamino-3,6-dichlorocarbazole as a versatile building block for the synthesis of anion receptors. Simple functionalization of the two amine side arms provides a preorganized binding site, which can be further stabilized by the hydrogen bond coming from the central NH of the carbazole.[13]

Herein we report the synthesis and evaluation of the H-bond properties of two novel sulfonamide carbazole receptors derived from 3,6-di-*tert*-butyl-9*H*-carbazole-1,8-disulfonic acid. Because the NHs are not directly linked to the carbazole platform, the geometry of these clefts is different from the ones previously reported.[13] The ability of these compounds to accommodate different anions has been studied by ^{1}H NMR and fluorescence titrations. X-ray structures of the pure receptors and some of their complexes have been obtained and the use of these compounds as fluorescent sensors has also been explored.

Results and discussion

Synthesis

Compounds **1** and **2** were prepared starting from the readily available 3,6-di-*tert*-butyl-9*H*-carbazole[14] (**3**) using straightforward procedures. The starting material shows high solubility in common organic solvents and due to the fact that positions 3 and 6 are substituted, sulfonation with chlorosulfonic acid in CH_2Cl_2 afforded the desired 3,6-di-*tert*-butyl-9*H*-carbazole-1,8-disulfonic acid in good yield (96%). The reaction of the acid (**4**) with PCl_5 yielded the corresponding sulfonyl chloride (**5**), which was reacted with the corresponding amines to afford the desired compounds (Scheme 1).

^{1}H NMR and fluorescence titrations

^{1}H NMR titrations in $CDCl_3$ were performed to explore the anion complexation properties of the carbazole based receptors. As expected, receptor **2** derived from 3,5 bis(trifluoromethyl)aniline showed a better affinity for the guests due to the H-bond activation by the CF_3 electron-withdrawing groups,[15] and this compound was chosen to carry out the main part of the assays.

The association constants are collected in Table 1. In all ^{1}H NMR measurements the concentration of the host was kept constant ($c = 2.5 \times 10^{-3}$ M) and increasing amounts of the guest were added until saturation was reached.

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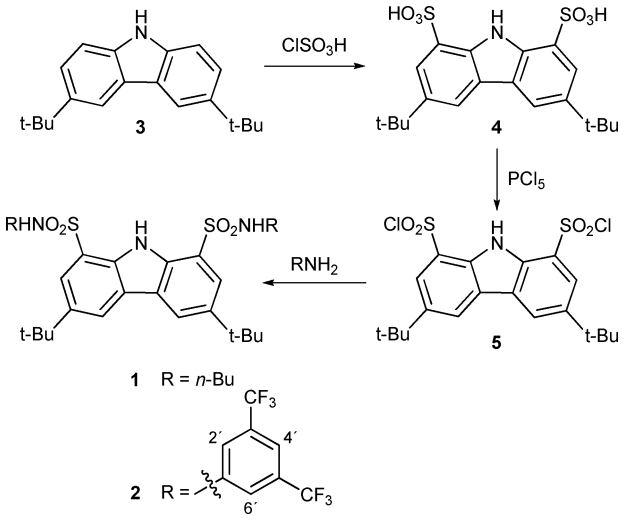
† Electronic supplementary information (ESI) available: Copies of NMR, IR and MS spectra of the compounds, selected binding curves, X-ray characterization data and modelling studies. CCDC reference numbers 832821–832825. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06126g



Scheme 1 Synthesis of receptors **1** and **2**.

Table 1 Association constants (M^{-1}) of the complexes formed by receptors **1** and **2** and several anions (added as tetrabutyl or tetraethyl ammonium salts) at 298 K in $CDCl_3$. Errors estimated to be ≤ 10%

Entry	Anion	Compound **1**	Compound **2**
1	Fluoride	—	2.2×10^{4a}
2	Chloride	3.7×10^{4}	7.9×10^{6b}
3	Bromide	4.5×10^{3}	1.1×10^{6c}
4	Iodide	—	4.2×10^{5c}
5	Hydrogen sulfate	—	8.8×10^{4a}
6	*m*-Nitrobenzoate	—	2.9×10^{4a}
7	Perchlorate	—	2.4×10^{3a}
8	Dihydrogen phosphate	—	[d]
9	Acetate	—	[d]

[a] Measured by ^{1}H NMR titration. [b] Measured by competitive fluorescence titration with bromide. [c] Measured by fluorescence. [d] Data could not be fitted to a 1 : 1 or 1 : 2 binding stoichiometry.

^{1}H NMR spectra did not provide evidence for the direct participation of the carbazole NH in the stability of the complexes. The chemical shift of the NH for the free receptors (singlet at 10.21 ppm for compound **1** and at 10.37 ppm for compound **2**) did not change upon addition of the guests. On the contrary, sulfonamide NH protons were strongly involved in binding as evidenced by the large complexation induced shifts (up to 3.33 ppm for compound **1** and 1.74 ppm for compound **2**). Also, the aromatic protons of the bis(trifluoromethyl)aniline unit were shifted during the titration ($\Delta\delta_{sat}$ = –0.34 ppm for H-4′) allowing us to estimate the association constants either by the sulfonamide NH or CH resonances (ESI Fig. S13†).

^{1}H NMR titration of receptor **2** with tetrabutylammonium fluoride in $CDCl_3$ yielded an association constant of 2.2×10^4 M^{-1} for the 1 : 1 complex. In the more polar solvent DMSO-d_6, a large excess of fluoride (10 : 1 anion to receptor ratio) led to deprotonation[16] with concomitant formation of the species $[HF_2]^-$, as evidenced by ^{1}H NMR (ESI Fig. S21†).

For the rest of the halides (Cl^-, Br^- and I^-), although the data indicated a very tight 1 : 1 binding in deuterochloroform (ESI Fig. S14†), the association constants could not be accurately determined by ^{1}H NMR.[17] Thus, the interaction of receptor **2** with these three halides was studied by fluorescence titration methods carried out at much lower concentrations. Fluorescence quenching titration curves of carbazole **2** (10 μM) with halides allowed calculation of an association constant of 4.2×10^5 M^{-1} for iodide (ESI Fig. S15–S16†). However, for bromide and chloride no binding curves could be obtained at this host concentration (ESI Fig. S17†) and more dilute solutions were then prepared (5 μM, 1 μM and 0.1 μM). While the association constant between **2** and TEABr was determined to be 1.1×10^6 M^{-1} (ESI Fig. S19†), the high affinity of receptor **2** for chloride did not allow measurement of an absolute constant and a competitive titration[18] was run, yielding an association constant of 7.9×10^6 M^{-1} (ESI Fig. S20†).

On the other hand, ^{1}H NMR titrations for chloride and bromide in the more competitive solvent DMSO-d_6 afforded, as expected, lower values of the association constants (K_a = 210 M^{-1} for chloride *vs.* K_a = 25 M^{-1} for bromide) but the selectivity trend was maintained. We also evaluated the binding ability of the receptor **2** towards DMSO in $CDCl_3$, affording an association constant of 710 M^{-1}, much lower than that reported for halides (Table 1, entries 2–3). Although receptor **2** bound halides preferentially over DMSO, with DMSO as solvent, the large molar DMSO : halide ratio strongly reduced the halide association constants (ESI Fig. S22–S24†).

Oxoanions such as hydrogen sulfate, *m*-nitrobenzoate and perchlorate were also tested, but in all cases ^{1}H NMR titrations (Table 1, entries 5, 6 and 7) revealed a strong decrease in affinity compared to the halide ions. Again, small shifts for the carbazole NH were observed during the titrations while sulfonamide NHs ($\Delta\delta_{sat}$ = 1.31 ppm) seemed to play the main role in binding (ESI Fig. S25†).

Titration with dihydrogen phosphate caused broadening of the carbazole and sulfonamide NH resonances, precluding an accurate determination of the association constant from these data. However, upfield shifts of the aromatic H-4′ resonance ($\Delta\delta$ = –0.28 and –0.35 ppm upon addition of 1 and 2 equiv., respectively) suggested strong binding, although the data could not be fitted to a binding isotherm as has already been reported by other authors.[19] Further evidence of phosphate binding came from the fact that receptor **2** was capable of extracting monohydrogen phosphate (as its diammonium salt) from an aqueous solution, when 18-crown-6-ether was present in the organic phase.

With the more basic anion acetate, the NH resonances disappeared completely during the titration, which might indicate deprotonation. Although the 3,5-bis(trifluoromethyl)phenyl proton resonances were visible along the titration, the data could not be fitted adequately to a binding model. In the fluorescence study (λ = 350 nm), the intrinsic blue fluorescence of the receptor **2** was quenched on addition of acetate; this effect is quite similar to that observed with added tetrabutylammonium hydroxide, and could be attributed to the basic character of the anions that deprotonates the receptor. Treatment with *p*-TsOH regenerated, in both cases, the initial fluorescence.

The association constants collected in Table 1 show the higher affinity of receptor **2** for the halides chloride, bromide and iodide, compared to the tested oxoanions. These results are unusual, and to our knowledge this preference has not been previously reported for H-bond anion receptors.[20] If the carbazole NH is not engaged in hydrogen bonding with the anions (as pointed out by the ^{1}H NMR data), the complexes with receptor **2** seem to be stabilized only by two hydrogen bonds with the sulfonamide

NHs. On the other hand, the well-known Schreiner's thiourea, with two hydrogen-bond donors, bound carboxylates with larger preference than halides as expected ($K_a = 1.4 \times 10^4$ M^{-1} for TBA *m*-nitrobenzoate *vs.* $K_a = 8.9 \times 10^3$ M^{-1} for TEACl, ESI Fig. S26†).

Therefore, to try to understand the reasons for this uncommon preference, X-ray analysis and modelling studies were carried out.

X-ray analysis

Slow evaporation of methylene chloride from a methylene chloride/cyclohexane solution of pure receptors allowed us to obtain crystals suitable for X-ray analysis (Fig. 1 and 2, ESI Fig. S27–S28†).

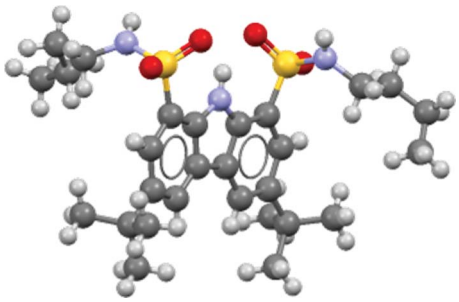


Fig. 1 X-ray structure of compound **1**.

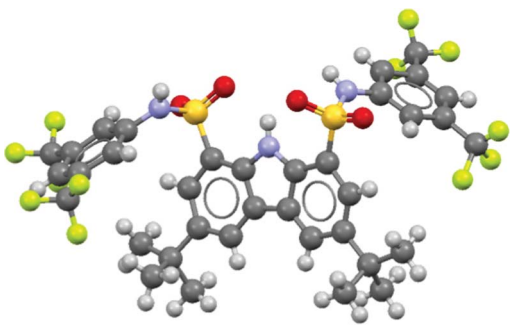


Fig. 2 X-ray structure of compound **2**.

X-ray diffraction analysis showed very similar conformations for both compounds. The central carbazole NH forms two intramolecular H-bonds, with $NH_{carbazole} \cdots O_{sulfonamide}$ distances of 2.949 Å and 2.995 Å for receptor **1** and 2.828 Å and 3.031 Å for receptor **2**. In both structures the distances between the two sulfonamide NHs of the side arms is too large ($N_{sulfonamide} \cdots N_{sulfonamide}$ = 6.676 Å) for the simultaneous formation of two H bonds with an anion.

The structures of the complexes formed between receptor **2** and tetraalkylammonium halides (chloride, bromide and iodide) were also solved by X-ray diffraction. Crystals of the 1 : 1 anion–receptor complexes were obtained by slow evaporation of CH_2Cl_2 from a methylene chloride/cyclohexane solution containing equimolar amounts of host and guest. However, attempts to grow crystals of the complexes with oxoanions, under the aforementioned conditions, were unsuccessful. Slow evaporation of the solvent from solutions of receptor **2** and *m*-nitrobenzoate, perchlorate, hydrogen sulphate or phosphate did not yield crystals of the complexes, affording only crystals of the pure receptor.

Fig. 3–5 (ESI Fig. S29–S31†) show the geometry of the complexes with chloride, bromide and iodide.

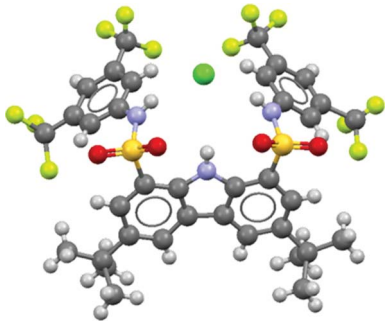


Fig. 3 X-ray crystal structure of **2**·TEACl. Tetraethylammonium counter cation was omitted for clarity.

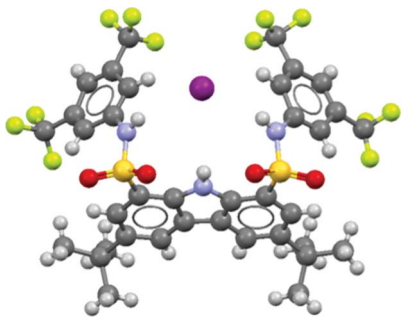


Fig. 4 X-ray crystal structure of **2**·TEABr. Tetraethylammonium counter cation was omitted for clarity.

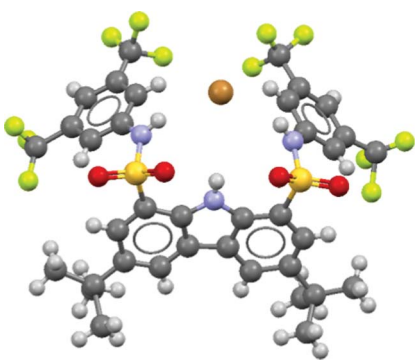


Fig. 5 The X-ray crystal structure of **2**·TBAI. Tetrabutylammonium counter cation was omitted for clarity.

Crystals of the complexes revealed a similar pattern with all the anions inside the carbazole cleft. The structures show that each halide is bound by two H-bonds, almost symmetrically disposed, with the sulfonamide NHs. The $NH_{sulfonamide} \cdots X$ (X = halide) lengths are 3.138 Å and 3.169 Å for the chloride, 3.290 Å and 3.294 Å for the bromide and 3.464 Å and 3.535 Å for the iodide (Table 2).

The complexes are further stabilized by two interactions with the aromatic CHs in positions 2′, with distances $CH \cdots X$ varying from 3.580 Å for the chloride to 3.654 Å for bromide and 3.769 Å for iodide. Searches of the Cambridge Structural Database[21] reveal

Table 2 Distances (Å) from the X-ray structures of receptor **2** and their complexes with halides (Cl, Br, I)

	$(N\cdots N)_{sulfonamide}$	$NH_{sulfonamide}\cdots X$	$CH\cdots X$	$NH_{carbazole}\cdots X$
2	6.676	—	—	—
2·TEACl	5.363	3.138/3.169	3.580	3.845
2·TEABr	5.555	3.290/3.294	3.654	3.963
2·TBAI	5.853	3.464/3.535	3.769	4.106

that such interactions between substituted benzene rings and anions (halides and oxoanions) are very common in the solid state.

In addition, in full agreement with the ^{1}H NMR data, the carbazole NH does not contribute to the binding as evidenced by the distances $NH_{carbazole}\cdots X$ in the range from 3.845 Å to 4.106 Å. The fact that the pyrrole NH is not involved in the recognition event is outstanding compared to other known X-ray structures for complexes between chloride and carbazole receptors[22] where this interaction is always one of the dominant ones.

Further stabilization of the complexes by anion–π interactions between halides and carbazole rings were not observed in the solid state (ESI Fig. 32†).

While the X ray analysis showed a good coincidence between receptor and halide geometries, it did not explain why oxoanions were not as suitable for this cleft, therefore a modelling study was started.

Modelling studies

A modelling study using the program Gaussian03[23] revealed the possible reasons for the lower affinity of receptor **2** for oxoanions.

Models of the complex of receptor **2** with chloride showed an almost perfect match with the X-ray structure (Fig. 6). The halide is bound in the complex by two H-bonds with the sulfonamide NHs ($NH_{sulfonamide}\cdots Cl$ distance of 3.2 Å). The computed distances for the intramolecular H-bonds ($NH_{carbazole}\cdots O_{sulfonamide}$ = 2.9 Å) and for the interactions $CH\cdots X$ (3.7 Å) are in excellent agreement with the X-ray diffraction measurements.

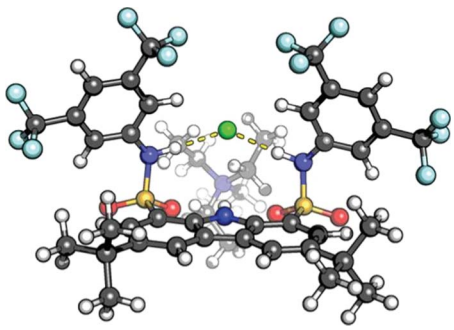


Fig. 6 Optimized structure of the complex between receptor **2** and TEACl (B3LYP/6-31G** level of theory).

In the case of oxoanions such as perchlorate or benzoate, where the oxygen atom has to be bound in the cleft, the calculated structures are quite similar to the one with chloride, with respect to H-bond lengths: $NH_{sulfonamide}\cdots O_{perchlorate}$ = 3.0 Å; $NH_{sulfonamide}\cdots O_{benzoate}$ = 2.9 Å; $NH_{carbazole}\cdots O_{sulfonamide}$ = 2.9 Å for both complexes. Taking into account the larger van der Waals radius for Cl (175 pm) *versus* O (152 pm), the H-bonds for the complex with the halide seem to be stronger than those formed with the oxygen atoms. But the explanation for the higher affinity for chloride ($K_a = 7.9\times10^6$ *vs.* 2.9×10^4 and 2.4×10^3) cannot rely only on this reason. A comparison between the computed structures with chloride and perchlorate allows us to establish another difference: as it is shown in Fig. 7, complexation with the oxoanion requires a more pronounced conformational change in the cleft reducing the $N_{sulfonamide}\cdots N_{sulfonamide}$ distance by more than 0.3 Å compared to the complex with chloride. This effect is enlarged at the top of the cleft where the separation between the carbons of the trifluoromethyl groups is reduced by more than 1 Å: $(C\cdots C)_{CF3}$ = 5.9 Å (complex with chloride) and $(C\cdots C)_{CF3}$ = 4.4 Å (complex with perchlorate), provoking steric hindrance between the fluorine atoms (distance $F\cdots F$ = 2.8 Å).

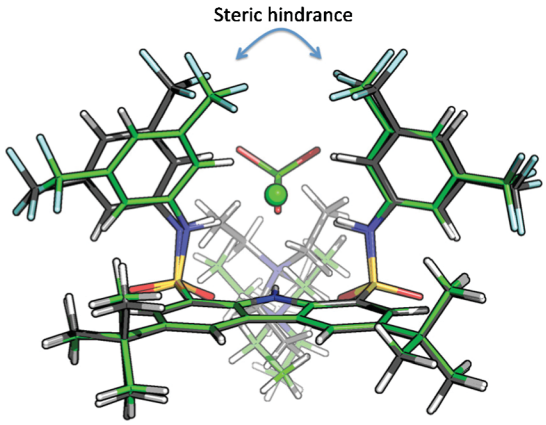


Fig. 7 Overlay of the optimized complex structures (B3LYP/6-31G**) between receptor **2** and TEACl (in grey) and $TEAClO_4$ (in green). In the perchlorate association complex, steric hindrance can be observed between the trifluoromethyl groups.

Conclusions

The readily available sulfonamide carbazole receptor **2** has shown a remarkably high affinity for halide anions, with the largest binding constant for chloride. According to the ^{1}H NMR data and supported by the X-ray structures, it is proposed that the complexes are stabilized by two H- bonds *via* the sulfonamide NHs and the other two $CH\cdots X$ interactions. In any case, the carbazole NH seems not to be involved in binding, keeping the same two intramolecular H-bonds already present in the free receptors. Surprisingly, oxoanions are not as good guests as halides for receptor **2**.

The conformational change associated with complex formation might be responsible for this behaviour. The two sulfonamide NH groups are far apart in the receptors and must be brought closer upon complexation. As modelling studies suggest, carboxylates and other oxoanions form complexes where the conformational change is more relevant. On the contrary, the larger halides are able to set two H-bonds with minor changes in the conformation, and so the binding process is more favoured.

Experimental

3,6-Di-*tert*-butyl-9*H*-carbazole-1,8-disulfonic acid (4). 3,6-di-*tert*-butyl-9*H*-carbazole[14] **3** (10.0 g, 35.82 mmol) was dissolved

in CH_2Cl_2 (200 cm^3) in a three necked flask equipped with a magnetic stirrer, a pressure-equalising dropping funnel and under argon atmosphere. The reaction mixture was cooled down to 0 °C in an ice bath. Then, a solution of chlorosulfonic acid (4.9 cm^3, 35.82 mmol) in methylene chloride (30 cm^3) was added dropwise with vigorous stirring. Once the addition was complete, the mixture was stirred for another half an hour and the reaction was monitored through ^1H NMR analysis of an aliquot. If starting material was still present, a few drops of chlorosulfonic acid in methylene chloride was added to the dropping funnel and stirring was continued until the reaction was complete. Then, the solvent was partially evaporated under reduced pressure until a solid began to precipitate. The reaction mixture was cooled down and the solid was filtrated to afford the crude disulfonic acid, which was used without further purification in the next step (15.13 g, 96%), mp 104–107 °C; (Found: C, 54.26; H, 5.75; N, 3.28; S, 14.55. $C_{20}H_{25}NO_6S_2$ requires C, 54.65; H, 5.73; N, 3.19; S, 14.59); ν_{max}(film/cm^{-1}) 3448, 1755, 1625, 1158 and 1054; δ_H (200 MHz, CD_3OD) 1.47 (18H, s), 7.96 (2H, d, *J* 2), 8.30 (2H, d, *J* 2); δ_C (50 MHz, CD_3OD) 31.2, 34.5, 119.1, 121.8, 124.2, 126.3, 134.0, 142.1; MS (ESI-) *m*/*z* 218.6.

3,6-Di-*tert*-butyl-N^1,N^8-dibutyl-9*H*-carbazole-1,8-disulfonamide (1). The disulfonic acid **4** (2.0 g, 4.55 mmol) was suspended in CH_2Cl_2 (10 cm^3) and cooled down in an ice bath. Then, PCl_5 (3.0 g, 14.4 mmol) was added and the reaction mixture was stirred until evolution of gas ceased. The ice bath was then removed and the reaction was stirred at room temperature until no more bubbles could be observed. ^1H NMR analysis of an aliquot showed no starting material. Then, the solvent was removed under reduced pressure to afford the corresponding sulfonyl chloride (**5**), which was used in the next reaction without further purification. Compound **5** (1.0 g, 2.1 mmol) in methylene chloride (10 cm^3) was treated with an excess of *n*-butylamine (1 cm^3, 10.5 mmol) and the mixture was stirred at room temperature. The reaction was monitored by TLC. Once the reaction was complete, the solvent was removed under reduced pressure and the crude residue was treated with 2 N HCl and extracted with ethyl acetate. The combined organic layers were dried over sodium sulphate, and the solvent was evaporated. Chromatography with CH_2Cl_2/EtOAc (95 : 5) afforded the pure compound **1** (1.04 g, 90%); mp 166–169 °C; (Found: C, 61.45; H, 7.73; N, 7.40; S, 11.30. $C_{28}H_{43}N_3O_4S_2$ requires C, 61.17; H, 7.88; N, 7.64; S, 11.66); ν_{max}(film/cm^{-1}) 3409, 1755, 1606, 1333, 1145 and 736; δ_H (200 MHz, $CDCl_3$) 0.72 (6H, t, *J* 6.8), 1.09–1.25 (4H, m), 1.28–1.39 (4H, m), 1.41 (18H, s), 2.91 (4H, q, *J* 6.8), 6.35 (2H, t, *J* 6.8, NH), 7.97(2H, d, *J* 1.8), 8.35 (2H, d, *J* 1.8), 10.19 (1H, s, NH); δ_C (50 MHz, $CDCl_3$) 13.6, 19.8, 31.2, 32.1, 35.2, 42.7, 121.6, 121.6, 124.6, 125.1, 134.1, 143.0; MS (ESI-) *m*/*z* 548.5, 584.5 $(M + Cl)^-$.

N^1,N^8-Bis(3,5-bis(trifluoromethyl)phenyl)-3,6-di-*tert*-butyl-9*H*-carbazole-1,8-disulfonamide (2). The disulfonic acid **4** was transformed into the sulfonyl chloride **5** following the same procedure described for the synthesis of compound **1**. Compound **5** (1.32 g, 2.78 mmol) and 3,5-(bis(trifluoromethyl)aniline (1.9 g, 8.29 mmol) were heated in pyridine (4 cm^3) at 90 °C for 2 h. The reaction was monitored by TLC. The solvent was evaporated and the residue was treated with 2 N HCl and extracted with EtOAc. The combined organic layers were dried (Na_2SO_4) and chromatography (CH_2Cl_2/EtOAc, 95 : 5) yielded the desired compound **2** (1.10 g, 46%); mp 121–124 °C; (Found: 50,03; H, 3.74; N, 4.73; S, 7.23. $C_{36}H_{31}F_{12}N_3O_4S_2$ requires C, 50.17; H, 3.63; N, 4.88; S, 7.44); ν_{max}(film/cm^{-1}) 3436, 3227, 1619, 1151, 989 and 898; δ_H (200 MHz, $CDCl_3$) 1.41 (18H, s), 7.58 (2H, s), 7.73 (4H, s), 8.00 (2H, d, *J* 1.8), 8.42 (2H, d, *J* 1.8), 9.69 (2H, s, NH), 10.22 (1H, s, NH); δ_C (50 MHz, $CDCl_3$) 31.7, 35.2, 118.3, 119.1, 119.3, 123.0 (q, $^1J_{CF}$ 271.9 Hz), 123.9, 125.5, 125.7, 133.2 (q, $^2J_{CF}$ 33.8 Hz), 133.8, 138.3, 144.3; MS (ESI-) *m*/*z* 860.4.

Acknowledgements

The authors thank the Spanish Dirección General de Investigación, Ciencia y Tecnología (DGI-CYT) (CTQ2010-19906/BQU) and the UE (European Re-integration Grant PERG04-GA-2008-239244) for their support in this work. The Spanish Ministerio de Educación (MEC) is acknowledged for the fellowship (A. L. F. A.). The authors are also grateful to Dr Mar López Blanco and Dr César Raposo.

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