Synthesis of bis(azafulvene)s by dehydration of hydroxymethylpyrrole derivatives

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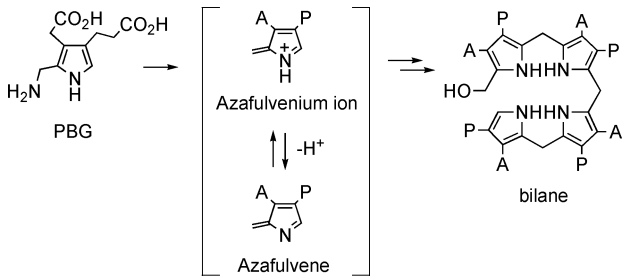
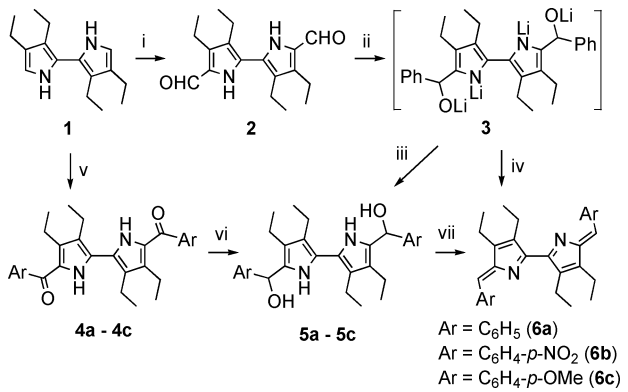
Bis(azafulvene) was isolated in 55% yield by the reaction of 4 equivalents of phenyllithium with 5,5′-diformyl-3,3′,4,4′-tetraethyl-2,2′-bipyrrole followed by quenching with acetic anhydride. Unstable bis(azafulvene)s were obtained in much higher yields by dehydrating 5,5′-bis(hydroxymethyl) derivatives of 2,2′-bipyrrole and *gem*-dimethyl-2,2′-dipyrrylmethane with $(Boc)_2O$–DMAP at room temperature. X-Ray crystallography of two bis(azafulvene)s is reported.

Introduction

Azafulvene has long appeared in the literature of pyrrole chemistry.[1–5] It was postulated as an intermediate in the nucleophilic substitution reactions at the 2-pyrrolylmethyl position and some trapping experiments of azafulvene have been reported.[1,2] However, neither parent azafulvene nor simple alkyl-substituted azafulvene has yet been isolated, although there have been known azafulvenes substituted with an amino group at the *exo*-double bond or involved in larger cyclic π-conjugation systems such as porphyrinoids.[5] Thus, the structure and properties of azafulvene have remained to be clarified in nonbenzenoid chemistry. Azafulvene is a conjugate base of the azafulvenium ion which is one of the most important intermediates for constructing porphyrinoids. It is usually generated from 2-(aminomethyl)pyrrole or 2-(hydroxymethyl)pyrrole derivatives under acid catalysis. It is believed that nature uses this strategy in the conversions from porphobilinogen (PBG) to (hydroxymethyl)bilane and then to uroporphyrinogen III (see Scheme 1).[6] However, undesired side reactions are frequently observed in the porphyrinoid synthesis under acidic conditions required to generate azafulvenium ions. For example, dipyrrylmethanes undergo acid-catalyzed decomposition to monomeric pyrroles with the intermediacy of azafulvenium ions.[7] Since azafulvene is of great importance not only as a fundamental member in nonbenzenoid chemistry but also due to its high potential in the synthesis of porphyrinoids under neutral conditions, a convenient preparative method for azafulvene is highly desired.



Scheme 1 Azafulvenium ion and azafulvene.



Scheme 2 Synthesis of bis(azafulvene)s. *Reagents*: i, DMF, $POCl_3$; ii, PhLi; iii, H_2O; iv, Ac_2O; v, $ArCONMe_2$, $POCl_3$; vi, $NaBH_4$; vii, $(Boc)_2O$, DMAP.

Results and discussion

Synthesis of bis(azafulvene)s

5,5′-Diformyl-3,3′,4,4′-tetraethyl-2,2′-bipyrrole **2** was reacted with phenyllithium (4 equiv.) at −70 °C and the resulting solution was quenched with acetic anhydride to give bis(azafulvene) **6a** in 55% yield.[8] This reaction is explained in terms of the *O*-acetylation of the tetraanionic intermediate **3** followed by elimination of acetate ion (see Scheme 2). Although the yield of **6a** is not high, quenching **3** with water instead of acetic anhydride gave the diol **5a** in 95% yield. Therefore, the *N*-acetylation of **3** or the instability of azafulvene under these strongly basic reaction conditions may be problematic. A new synthetic method allowing preparation of azafulvene with functional groups is of great importance, because azafulvene is a unique precursor for functional materials based on the porphyrinoid structure. As bis(azafulvene) is a dehydrated form of the diol, it occurred to us to examine some reactions of the diol with dehydrating reagents. When **5a** was allowed to react with di-*tert*-butyl dicarbonate (2.5 molar equiv.) under the catalysis of *N*,*N*′-dimethylaminopyridine (5 mol%) at room temperature in 2 h, **6a** was obtained in 92% yield. Scope of this new azafulvene synthesis would be expanded if diols with various functional groups were available without using

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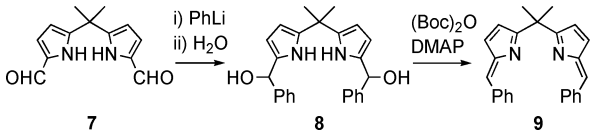
organolithium reagents. Thus, 3,3′,4,4′-tetraethyl-2,2′-bipyrrole **1** was converted into 5,5′-bis(*p*-nitrobenzoyl)-3,3′,4,4′-tetraethyl-2,2′-bipyrrole **4b** in 86% yield by using Vilsmeier-type aroylation.[9] Then, **4b** was reduced quantitatively to the corresponding diol **5b** with $NaBH_4$ according to the procedure used for 5,5′-diaroyl-2,2′-dipyrrylmethanes by Lindsey and co-workers.[10] Dehydration of **5b** proceeded smoothly with $(Boc)_2O$–DMAP in CH_2Cl_2 at room temperature for 1.5 h to give 83% yield of bis(azafulvene) **6b**. This aroylation–reduction–dehydration sequence afforded bis(azafulvene) **6c** having *p*-methoxyphenyl substituents in 70% overall yield from **1**. This dehydration reaction worked well for the diol **8** derived from *gem*-dimethyldipyrrylmethane to give *gem*-dimethylbis(azafulvenyl)methane **9** in 98% yield (see Scheme 3). The one-pot procedure of adding phenyllithium to dialdehyde **7** followed by quenching with Ac_2O did not work well, because **9** formed in a lower yield, was difficult to precipitate and was degraded during purification procedures.



Scheme 3 Synthesis of bis(azafulvenyl)methane.

^1H and ^{13}C NMR chemical shifts of bis(azafulvene)s, **6a** and **9**, assigned on the basis of the 2D CH-correlation experiments are summarized in comparison with those of the corresponding diols, **5a** and **8**, in Table 1. Large chemical shift changes observed for the methine carbon and the methine proton clearly indicate the hybridization change from sp^3 for diol to sp^2 for bis(azafulvene). It is remarkable that the chemical shift of one of the pyrrole-α carbons is shifted by *ca.* 50 ppm to the higher frequency region upon going from diol to bis(azafulvene). This is indicative of the electron deficient character of bis(azafulvene)s. The chemical shift due to the phenyl *ortho*-proton of bis(azafulvene) is also in the remarkably high frequency region, which is diagnostic of the formation of bis(azafulvene).

Dehydration reaction

^1H NMR monitoring of the dehydration reaction of **5b** with $(Boc)_2O$–DMAP in $CDCl_3$ indicated that conversion from **5b** to an alkyl carbonate intermediate was completed within a few minutes at room temperature as shown in Fig. 1(b). This is supported by the disappearance of the OH signal at 2.25 ppm and the high

Table 1 Selected NMR chemical shifts (δ_H and δ_C) of bis(azafulvene)s (**6a**, **9**) and diols (**5a**, **8**) in $CDCl_3$ at 20 °C

	5a		**6a**		**8**		**9**	
Position	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
Pyrrole-α	120.4	—	168.8	—	134.2	—	182.3	—
Pyrrole-β	122.5	—	141.7	—	102.7	5.69	126.9	6.62
Pyrrole-β′	122.8	—	147.6	—	106.5	5.98	139.2	7.06
Pyrrole-α′	128.0	—	154.8	—	141.8	—	155.0	—
Methine	68.2	5.95	131.5	6.98	69.2	5.31	134.7	6.89
Phenyl-*ipso*	142.2		135.9		141.2		135.4	
Phenyl-*ortho*	128.6	7.40	133.0	8.33	128.0	7.32	133.1	8.34
Phenyl-*meta*	126.1	7.36	128.5	7.42	126.2	7.29	128.9	7.43
Phenyl-*para*	127.6	7.28	129.9	7.38	127.4	7.27	130.2	7.38

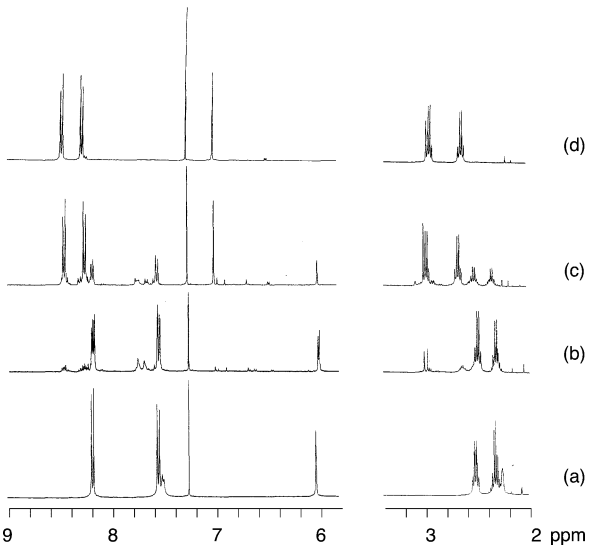
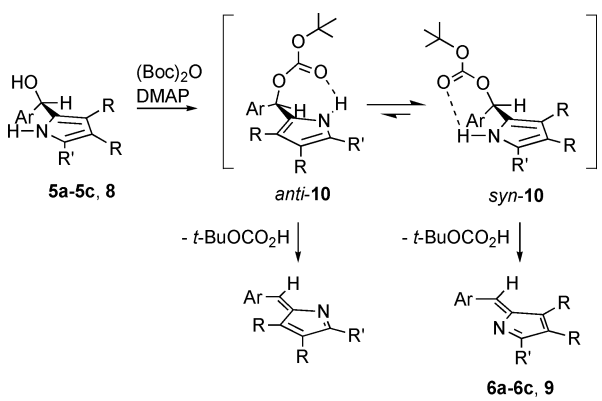


Fig. 1 ^1H NMR spectral changes by the addition of $(Boc)_2O$ (2.5 equiv.)–DMAP (5 mol%) to **5b** in $CDCl_3$: (a) before addition; (b) just after addition; (c) 50 min after addition; (d) 100 min after addition.

frequency shift of the NH signal at 7.5 ppm to two signals at 7.65 and 7.70 ppm. This signal splitting means that the magnetic nonequivalence of a *meso* form and a (±)-form is enhanced by the carbonation of the hydroxyl group of **5b**. The alkyl carbonate was a transient species and gradually changed to **6b** in 2 h at room temperature. Remarkably high frequency chemical shifts at 7.01 ppm of the methine proton next to the phenyl group of **6b** is characteristic of azafulvene.

This smooth reaction from the alkyl carbonate intermediate to bis(azafulvene) can be explained in terms of a seven-membered cyclic transition state which facilitates proton transfer from the pyrrole nitrogen to the carbonyl oxygen in conjugation with electron flow from the pyrrole π-bonding orbital to the anti-bonding σ*-orbital of the C–O bond (see Scheme 4). The overlap of these two orbitals is a stereoelectronic requirement for this elimination reaction. Steric repulsion between the aryl group and the pyrrole β-position drives equilibrium between two possible conformations, *syn*-**10** and *anti*-**10**, of the cyclic transition state to one side. This results in the formation of bis(azafulvene)s with the *syn*-relationship of the aryl group and the pyrrole nitrogen, which was confirmed by X-ray crystallographic analysis



Scheme 4 Synthesis of bis(azafulvenyl)methane.

as shown in Fig. 2 and Fig. 3. It is remarkable that predominance of *syn*-**10** over *anti*-**10** is retained even if the β-pyrrole position is not substituted. However, the *syn–anti* isomerization of **9** occurred at room temperature in several hours in solution, when additional signals due to isomer(s) were observed at 7.08 and 6.59 ppm for the β-pyrrole protons, at 6.91 ppm for the methine proton, and at 1.80 ppm for CH_3 in $CDCl_3$. The presence of the ethyl group at the β-pyrrole position prohibited this isomerization in the cases of **6a–6c**. The observed stereoselective formation of *syn*-**9** and the subsequent *syn–anti* isomerization argue for the cyclic transition state in the carbonate elimination as shown in Scheme 4 because a simple S_N1-like pathway would directly lead to a mixture of *syn*-**9** and *anti*-**9**.

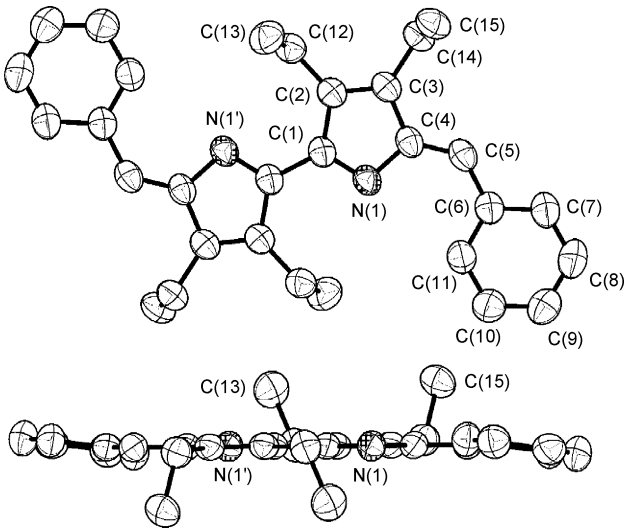


Fig. 2 ORTEP drawings of **6a** with 50% thermal ellipsoids and atom numbering scheme; a top view (top) and a side view (bottom). N(1′) is at equivalent position $(1 - x, -y, 1 - z)$.

X Ray crystal structures

Fig. 2 shows the X-ray structure of **6a** where the molecule lies about an inversion center. Therefore, the N–C_α–C_α–N torsion angle of **6a** is exactly 180°. The phenyl ring is tilted by 8.36° with respect to the pyrrole plane. Thus, **6a** is a planar molecule allowing effective π-conjugation. Fig. 3 shows the X-ray structure of **9** where the molecule lies with its central carbon atom C(12) on a

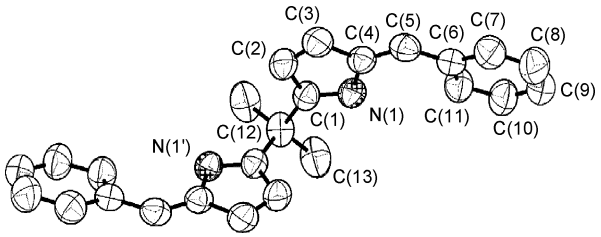


Fig. 3 ORTEP drawings of **9** with 50% thermal ellipsoids and atom numbering scheme. N(1′) is at equivalent position $(1 - x, -y, z)$.

crystallographic twofold axis. The angle between the mean pyrrole plane and the mean phenyl plane is 16.90° in the case of **9**. The bond alternation in the azafulvene structure is seen by the single bond character for the C_α–C_β bonds (1.481 and 1.469 Å for **6a**; 1.456 and 1.447 Å for **9**) and the double bond character for the C_β–C_β bond (1.349 Å for **6a**; 1.331 Å for **9**) of the pyrrole ring, which is in contrast to the structure of normal pyrrole (1.357 Å for the C_α–C_β bond; 1.423 Å for the C_β–C_β bond).[11] The distance of the *exo* double bond (1.351 Å for **6a** and 1.350 Å for **9**) is very similar to that reported for dimethylfulvene $Me_2C{=}C(CH{=}CH)_2$ (1.344 Å) and phenylfulvene $PhCH{=}C(CH{=}CH)_2$ (1.362 Å) (Table 2).[12,13]

Conclusions

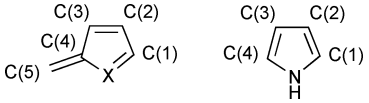
Azafulvene derivatives not stabilized by heteroatom substitution were obtained for the first time and their X-ray structures were presented here. Bis(azafulvene) and bis(azafulvenyl)methane described here are regarded as the best known models for understanding the parent azafulvene structure. We have developed a versatile synthetic method for bis(azafulvene)s through the dehydration of 2-(hydroxymethyl)pyrrole derivatives with $(Boc)_2O$–DMAP. The bis(azafulvene)s having functional groups were prepared in good yields to illustrate the utility of this synthetic method. These compounds are of interest, since bis(azafulvene) can react with α-free pyrroles under neutral conditions without using catalyst to give porphyrinoids.[8]

Experimental

General

Melting points were measured with a YANACO micro melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded

Table 2 Selected bond lengths (Å) with e.s.d.s of **6a** and **9** in comparison with those of pyrrole, dimethylfulvene and phenylfulvene[a]



Bond	**6a**	**9**	Pyrrole[b]	Dimethyl-fulvene[c]	Phenyl-fulvene[d]
C(1)–C(2)	1.481 (2)	1.456 (3)	1.357	1.435	1.455
C(2)–C(3)	1.349 (2)	1.331 (3)	1.423	1.346	1.341
C(3)–C(4)	1.469 (2)	1.447 (3)	1.357	1.440	1.468
C(4)–C(5)	1.351 (2)	1.350 (3)	—	1.344	1.362
X(1)–C(1)	1.310 (2)	1.306 (2)	1.365	1.346	1.359
X(1)–C(4)	1.404 (2)	1.404 (3)	1.365	1.440	1.463

[a] X = N for **6a** and **9**; X = CH for dimethylfulvene and phenylfulvene. [b] Taken from ref. 11. [c] Taken from ref. 12. [d] Taken from ref. 13.

on a Varian Inova 400 spectrometer (400 MHz). Chemical shifts were referenced with respect to $(CH_3)_4Si$ (0 ppm) and $CDCl_3$ (77.05 ppm) as an internal standard. The UV-visible spectra were measured on a JASCO V-570 spectrometer. Elemental analyses of C, H, and N were made with a YANACO MT-5 CHN recorder. EI-MS spectra were measured with a Shimadzu QP-2000A mass spectrometer. Solvents were purified prior to use by conventional methods. $CDCl_3$ was passed through basic Al_2O_3 before use. Other chemicals were of reagent grade and used as received. 5,5′-Diformyl-3,3′,4,4′-tetraethyl-2,2′-bipyrrole **2** and 5,5′-diformyl-*gem*-dimethyldipyrrylmethane **7** were synthesized according to the literature method.[14]

5,5′-Bis(phenylhydroxymethyl)-3,3′,4,4′-tetraethyl-2,2′-bipyrrole (5a)

Phenyllithium (8.8 mmol; 1 mol L^{-1} solution in cyclohexane–diethyl ether) was added dropwise to a dry THF solution (30 mL) of the dialdehyde **2** (1.66 mmol) at −50 °C under argon. The color changed from orange to brown. After the reaction mixture was stirred at −50 °C for 2.5 h, it was gradually warmed to room temperature in 1 h and stirring was continued for a further 1 h at room temperature. The deep brown solution was quenched with water (20 mL) showing a color change to purple and then yellow. The reaction mixture was repeatedly extracted with diethyl ether. The organic layer was washed with water and then with brine. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the residue was precipitated by adding hexane to a cold diethyl ether solution to give **5a** as a brown powder. Yield 95% (obtained as a mixture of a *meso* form and a ± form). Mp 138–140 °C. NMR δ_H ($CDCl_3$) 7.53 (br, 2H), 7.4–7.2 (m, 10H), 5.95 (s, 2H), 2.52 (q, 4H), 2.32 (q, 4H), 2.07 (s, 2H), 1.11 (t, 6H) and 0.97 (t, 6H); δ_C ($CDCl_3$) 142.2, 128.6, 128.0, 127.6, 126.1, 122.8, 122.5, 120.4, 68.2, 17.9, 17.4, 16.8 and 16.3. MS (EI) m/z 438 ($M^+ - H_2O$) and 420 ($M^+ - 2H_2O$). Elemental analysis, calcd (%) for $C_{30}H_{36}N_2O_2$: C, 78.91; H, 7.95; N, 6.13. Found: C, 78.78; H, 8.07; N, 6.00.

6,6′-Diphenyl-3,3′,4,4′-tetraethyl-2,2′-bis(azafulvene) (6a)

Phenyllithium (8.4 mmol; 1 mol L^{-1} solution in cyclohexane–diethyl ether) was added dropwise to a dry THF solution (30 mL) of the dialdehyde **2** (1.68 mmol) at −50 °C under argon. After the reaction mixture was stirred at −50 °C for 2.5 h, it was gradually warmed to room temperature in 1 h and stirring was continued for further 1 h at room temperature. To the deep brown solution were added triethylamine (10.0 mmol) and then acetic anhydride (8.4 mmol). After stirring for 30 min, water (20 mL) and hexane (20 mL) was added and the reaction mixture was partitioned. The organic layer was washed with brine and then dried over anhydrous K_2CO_3. The solvent was removed under reduced pressure and the residue was washed with methanol to give **6a** as brown powder. Yield 55%. Mp 170–175 °C. NMR δ_H ($CDCl_3$) 8.33 (d, 4H), 7.44–7.37 (m, 6H), 6.98 (s, 2H), 3.01 (q, 4H), 2.65 (q, 4H), 1.28 (t, 6H) and 1.24 (t, 6H); δ_C ($CDCl_3$) 168.8, 154.8, 147.6, 141.7, 135.9, 133.0, 131.5, 129.9, 128.5, 19.4, 17.7, 16.8 and 15.2. MS (EI) m/z 420 (M^+). Elemental analysis, calcd (%) for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66. Found: C, 85.75; H, 7.93; N, 6.44. UV-Vis (λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 414 (4.07×10^4).

5,5′-Bis(*p*-nitrobenzoyl)-3,3′,4,4′-tetraethyl-2,2′-bipyrrole (4b)

N,*N*′-Dimethyl-*p*-nitrobenzamide (5.0 mmol) was dissolved in $POCl_3$ (7.5 mmol) at 45 °C under argon and the solution was stirred for 24 h at room temperature. 3,3′,4,4′-Tetraethyl-2,2′-bipyrrole (0.85 mmol) dissolved in dry dichloroethane (5 ml) was added at once to the above solution. After the resulting reaction mixture was stirred at room temperature for 30 h, saturated K_2CO_3 aqueous solution was added carefully and the two-phase mixture was stirred for 15 min at room temperature and then for 3 h at reflux. The organic layer was separated, washed with water, dried over K_2CO_3, and evaporated to give red oil. Silica gel flush column with CH_2Cl_2–diethyl ether (10 : 1) gave **4b** as a light yellow powder. Yield 86%. Mp 238–240 °C. NMR δ_H ($CDCl_3$) 8.91 (s, 2H), 8.36 (d, 4H, $J = 8.8$ Hz), 7.84 (d, 4H, $J = 8.8$ Hz), 2.56 (q, 4H), 2.47 (q, 4H), 1.12 (t, 6H) and 1.01 (t, 6H). MS (EI) m/z 542 (M^+). Elemental analysis, calcd (%) for $C_{30}H_{30}N_4O_6$: C, 66.41; H, 5.57; N, 10.33. Found: C, 66.09; H, 5.47; N, 10.26.

5,5′-Bis(*p*-nitrophenyl(hydroxy)methyl)-3,3′,4,4′-tetraethyl-2,2′-bipyrrole (5b)

$NaBH_4$ (9.40 mmol) was added in portions to a solution of **4b** (0.18 mmol) in THF–methanol (1 : 1, 12 ml) under argon. The mixture was stirred at room temperature for 3 h, then it was partitioned between water and CH_2Cl_2. The organic layer was washed with water, dried over K_2CO_3, and evaporated. Crystallization from CH_2Cl_2–hexane afforded **5b** as an orange powder. Yield 98% (obtained as a mixture of a *meso* form and a ± form). NMR δ_H ($CDCl_3$) 8.20 (d, 4H, $J = 8.8$ Hz), 7.56 (d, 4H, $J = 8.8$ Hz), 7.52 (br, 2H), 6.03 (s, 2H), 2.52 (q, 4H), 2.32 (q, 4H), 2.25 (s, 2H), 1.13 (t, 6H) and 0.97 (m, 6H). Elemental analysis, calcd (%) for $C_{30}H_{34}N_4O_6$: C, 65.92; H, 6.27; N, 10.25. Found: C, 65.83; H, 6.43; N, 10.38.

6,6′-Di-*p*-nitrophenyl-3,3′,4,4′-tetraethyl-2,2′-bis(azafulvene) (6b)

To a mixture of the diol **5b** (0.17 mmol) and 4-dimethylaminopyridine (0.009 mmol) was added a dry CH_2Cl_2 solution (14 ml) of di-*tert*-butyl dicarbonate (0.44 mmol) under argon. After stirring for 1.5 h at room temperature, the color of the solution turned from orange to red. Hexane (30 ml) was added and the mixture was condensed to make complete precipitation of **6b**. Yield 83%. Mp 234 °C (decomposed). NMR δ_H ($CDCl_3$) 8.45 (d, 4H, $J = 9.0$ Hz), 8.26 (d, 4H, $J = 9.0$ Hz), 7.01 (s, 2H), 2.97 (q, 4H), 2.66 (q, 4H), 1.25 (t, 6H) and 1.27 (t, 6H). MS (EI) m/z 510 (M^+). Elemental analysis, calcd (%) for $C_{30}H_{30}N_4O_4$: C, 70.57; H, 5.92; N, 10.97. Found: C, 70.63; H, 5.93; N, 10.99.

5,5′-Bis(*p*-methoxybenzoyl)-3,3′,4,4′-tetraethyl-2,2′-bipyrrole (4c)

Yield 84%. Mp 100–102 °C. NMR δ_H ($CDCl_3$) 8.66 (s, 2H), 7.73 (d, 4H, $J = 8.8$ Hz), 6.98 (d, 4H, $J = 8.8$ Hz), 3.89 (s, 6H), 2.68 (q, 4H), 2.57 (q, 4H) and 1.11 (m, 12H). MS (EI) m/z 512 (M^+). Elemental analysis, calcd (%) for $C_{32}H_{36}N_2O_4$: C, 74.97; H, 7.08; N, 5.46. Found: C, 75.19; H, 7.48; N, 5.17.

5,5′-Bis(*p*-methoxyphenyl(hydroxy)methyl)-3,3′,4,4′-tetraethyl-2,2′-bipyrrole (5c)

Unstable compound obtained as a mixture of a *meso* form and a ± form. δ_H ($CDCl_3$) 7.60 (s, 2H), 7.30 (d, 4H, $J = 8.8$ Hz), 6.87 (d, 4H, $J = 8.8$ Hz), 5.90 (s, 2H), 3.79 (s, 6H), 2.49 (m, 4H), 2.33 (q, 4H), 2.12 (br, 2H), 1.11 (t, 6H) and 0.98 (m, 6H).

6,6′-Di-*p*-methoxyphenyl-3,3′,4,4′-tetraethyl-2,2′-bis(azafulvene) (6c)

Yield 85% (overall from **4c**). Mp 192–194 °C. NMR δ_H ($CDCl_3$) 8.33 (d, 4H, $J = 9.3$ Hz), 6.94 (d, 4H, $J = 9.3$ Hz), 6.93 (s, 2H), 3.88 (s, 6H), 3.02 (q, 4H), 2.64 (q, 4H), 1.28 (t, 6H) and 1.23 (t, 6H). MS (EI): m/z 480 (M^+). Elemental analysis, calcd (%) for $C_{32}H_{36}N_2O_2 \cdot H_2O$: C, 77.08; H, 7.68; N, 5.62. Found: C, 76.68; H, 7.61; N, 5.43.

***gem*-Dimethyl-5,5′-bis(phenyl(hydroxy)methyl)-2,2′-dipyrrylmethane (8)**

Phenyllithium (18.8 mmol; 1 mol L^{-1} solution in cyclohexane–diethyl ether) was added dropwise to a dry THF solution (26 ml) of 5,5′-diformyl-*gem*-dimethyldipyrrylmethane **7** (2.31 mmol) cooled at −65 °C under argon. After stirring for 1.5 h at −65 °C and then for 1.5 h at room temperature, water (10 ml) was added. The reaction mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over anhydrous K_2CO_3. Hexane was added to the diethyl ether solution and then condensation under reduced pressure gave white precipitates. Yield 95% (obtained as a mixture of a *meso* form and a ± form). Mp 126–130 °C. NMR (a major component) δ_H ($CDCl_3$) 10.00 (br, 2H), 7.35–7.25 (m, 10H), 5.98 (t, 2H, $J = 3.0$ Hz), 5.69 (t, 2H, $J = 3.0$ Hz), 5.31 (d, 2H, $J = 7.1$ Hz), 1.94 (d, 2H, $J = 7.4$ Hz) and 1.59 (s, 6H); δ_C ($CDCl_3$) 141.8, 134.2, 106.5, 102.7, 141.2, 128.0, 127.4, 126.2, 69.2, 36.1 and 30.2. MS (EI) m/z 350 ($M^+ - 2H_2O$). Elemental analysis, calcd (%) for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.91; H, 7.07; N, 7.11.

6,6′-Diphenyl-2,2′-bis(azafulvenyl)-*gem*-dimethylmethane (9)

To a mixture of the diol **8** (0.53 mmol) and 4-dimethylaminopyridine (0.028 mmol) was added a dry ether solution (8 ml) of di-*tert*-butyl dicarbonate (1.57 mmol) under argon. After stirring for 3 h at room temperature, the color of the solution turned bright yellow. Aqueous K_2CO_3 solution (8 mL, 0.02 mol L^{-1}) was added to the reaction mixture and it was extracted with diethyl ether. After drying over anhydrous K_2CO_3, hexane (5 ml) was added to the ether solution and condensed under reduced pressure. A small amount of precipitate formed at first and was removed by filtration and the filtrate was evaporated to give an oily substance **9**. It was solidified by storing in a refrigerator at −20 °C. Yield 98%. NMR δ_H ($CDCl_3$) 8.33 (d, 4H), 7.43 (t, 4H) 7.38 (t, 2H), 7.06 (d, 2H, $J = 4.5$ Hz), 6.89 (s, 2H), 6.62 (d, 2H, $J = 4.5$ Hz) and 1.82 (s, 6H); δ_C ($CDCl_3$) 182.3, 154.9, 139.2, 126.9, 135.4, 133.1, 130.2, 128.9, 134.7, 42.5 and 24.9. MS (EI) m/z 350 $(M)^+$. Elemental analysis, calcd (%) for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.48; H, 6.39; N, 8.17. UV-Vis (λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 350 (4.07×10^4).

X-Ray crystallography

A Bruker Smart 1000 diffractometer equipped with a CCD detector was used for data collection. An empirical absorption correction was applied using the SADABS program. The structure was solved and refined by full-matrix least-squares calculations on F^2 using the SHELXTL 97 program package.[15] **6a** was recrystallized by slow evaporation of a solution of CH_2Cl_2–acetone: $C_{30}H_{32}N_2$, $M = 420.58$, orthorhombic, space group *Pbca*, $a = 14.883(4)$, $b = 7.830(2)$, $c = 20.587(3)$ Å, $V = 2399.0(11)$ Å^3, $Z = 4$, $D_{calc} = 1.164$ g cm^{-3}, μ(Mo-Kα) = 0.067 mm^{-1}, $T = 294(2)$ K, crystal size 0.20 × 0.20 × 0.20 mm. A total of 2409 unique reflections were collected ($4.0 < 2\theta < 53.9°$) using graphite-monochromated Mo-Kα radiation. After structure solution by the direct method, 209 parameters were refined for all non-hydrogen atoms anisotropically and all hydrogen atoms isotropically. $R_1 = 0.0410$, $wR_2 = 0.977$ for 1472 reflections with $I > 2.00\sigma(I)$; $R_1 = 0.0793$, $wR_2 = 0.1166$ for all data. GOF (on F^2) = 1.010. **9** was recrystallized by slow evaporation of a solution of THF–hexane: $C_{25}H_{22}N_2$, $M = 350.45$, orthorhombic, space group *Fdd2*, $a = 17.135(3)$, $b = 38.228(8)$, $c = 6.1877(12)$ Å, $V = 4053.1(14)$ Å^3, $Z = 8$, $D_{calc} = 1.149$ g cm^{-3}, μ(Mo-Kα) = 0.067 mm^{-1}, $T = 295(2)$ K, crystal size 0.45 × 0.20 × 0.05 mm. A total of 2076 unique reflections were collected ($4.3 < 2\theta < 54.6°$) using graphite-monochromated Mo-Kα radiation. After structure solution by the direct method, 167 parameters were refined for all non-hydrogen atoms anisotropically and all hydrogen atoms isotropically. $R_1 = 0.0392$, $wR_2 = 0.0884$ for 1359 reflections with $I > 2.00\sigma(I)$; $R_1 = 0.0749$, $wR_2 = 0.1039$ for all data. GOF (on F^2) = 1.008. CCDC reference numbers 294434 and 294435. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518340e.

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