Keynote Article*

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Studies in the cycloproparene series;[1] heterocyclic substituted methylidenecyclopropa[*b*]naphthalenes

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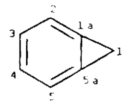
1*H*-Cyclopropa[*b*]naphthalene **7** is converted into a range of 6π 5-atom-substituted methylidene derivatives **12e–j**, the pyridyl analogues **12k** and **l**, and the phenylsulfanyl analogue **12m** by way of the 1,1-disilyl compound **9** and Peterson olefination in improved procedure. The spectroscopic properties of the compounds are reported and their behaviour as possible lumophores assessed. Crystal structures of the dimethylaminophenyl **12c,d**, and the thienyl **12e** derivatives are presented. The permanent dipole moments of the mono-substituted **12e** and **k** have been measured as 2.76, and 3.37 D, respectively, and that of the dithenyl **12f** as 9.06 D.

Cycloproparenes and their derivatives

The class of strained aromatic hydrocarbons known as the cycloproparenes,[2,3] and illustrated by the parent molecule 1*H*-cyclopropabenzene† **1**,[4] has provided a wealth of fascinating chemistry in the 30 years since the first authenticated derivative was reported.[5] While the hydrocarbons are strained[6] by about 290 kJ mol^{-1}, the imposition of additional strain to the extent of *ca.* 420 kJ mol^{-1} has been accomplished from generation of the cyclopropabenzynes **2** and **3** by dehydrobromination methodology; they were intercepted at ambient temperature by Diels–Alder cycloaddition to furan.[7] More recently, all of the known small-ring fused benzenoid hydrocarbons have been characterised crystallographically. Sophisticated studies involving collaborations between Boese and the groups of Billups, Neidlein and Vollhardt have provided the essential data for **1** and **4–6**, respectively.[8] From the geometrical parameters and difference electron density maps, it is clear that the fusion of a strained ring to a benzenoid nucleus results in the formation of bent 'banana' bonds about the sites of fusion with the consequence that internuclear distances, in themselves, can be misleading. Furthermore, if any bond length alternation is present, it is small and of little chemical significance. This fact is of prime importance in any consideration of the 'Mills-Nixon' effect[9] which implies that the fusion of a small strained ring to a benzenoid nucleus will result in an alternation of the bond lengths in the aromatic ring. Despite these and other elegant studies by Stanger[10] and Baldridge and Siegel[11] the debate over the Mills–Nixon effect has not yet abated.[12,13]



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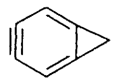

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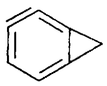

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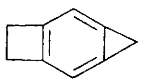

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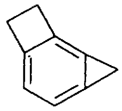

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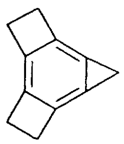

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Although rocketene **4**[14] and its angular isomer **5**[15] are comparatively easy to prepare, neither of the two possible dicyclopropabenzenes are known.[2] In comparison, the fusion of a three-membered ring to separate rings of naphthalene,[16] anthracene and phenanthrene, and derivatives[17] has been achieved, and triscycloproparenes which have three cyclopropabenzenoid moieties have now been reported[18] (Fig. 1). Not only has a wide range of cycloproparene structural types been prepared but also the chemistry has been subjected to assessment. This has formed the basis of a recent account[2] and consequently all that can be justified here is mention of the fact that the HOMO of the cyclopropabenzene lies between C-1a and C-5a (the bridge bond), and C-3 and C-4. As a family, the compounds act as excellent benzylating agents by way of electrophilic opening of the three-membered ring either directly, with cleavage of the σ bond from silver(I) catalysis, or *via* initial addition of the electrophile to the π framework and subsequent opening of the three-membered ring. Cycloadditions have also been effected and both the bridge bond and the strained cyclopropene σ bond can be involved (Scheme 1).[2,19,20] Additions to the bridge bond occur primarily with cyclopropabenzene **1** and they have resulted in a range of derivatives that transform into other interesting compounds. In comparison, cyclopropa[*b*]naphthalene **7** predominantly opens the three-membered ring by σ bond addition thereby avoiding a high energy orthoquinodimethane intermediate.[20]

Apart from the neutral molecules, chemistry involving the C-1 cycloproparenyl cation is well established,[2,21] but the derived radical is unknown.[22] In comparison, the C-1 cyclopropabenzenyl anion has been the subject of physicochemical scrutiny (the pK_a of **1** is estimated[23] as *ca.* 36) and it and its cyclopropa[*b*]naphthalenyl analogue **8** can be generated and used in synthesis.[24–26] Indeed, it is through use of these C-1 anions, *e.g.* **8**, that the range of unusual alkylidenecycloproparenes, *e.g.* **12**, has become available by way of transformation into α-silyl anions, *e.g.* **10**, that undergo Peterson olefination with a range of non-enolisable aldehydes or ketones (path *a*, Scheme 2).[2,24–26] More recently, it has been found that acylation of the α-silyl anion **10** gives a 1-acyl-1-trimethylsilyl derivative **11** that can subsequently interact with a nucleophile and provide an alkylidene derivative in a complementary pathway (path *b*, Scheme 2).[26] The scope and limitations of this route have yet to be established.

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† IUPAC and the Chemical Abstracts Service are unanimous in naming **1** as bicyclo[4.1.0]hepta-1,3,5-triene whereas with **7** cyclopropa fusion nomenclature applies. For the convenience of comparisons the ring system **1** is named in the text as 1*H*-cyclopropabenzene.

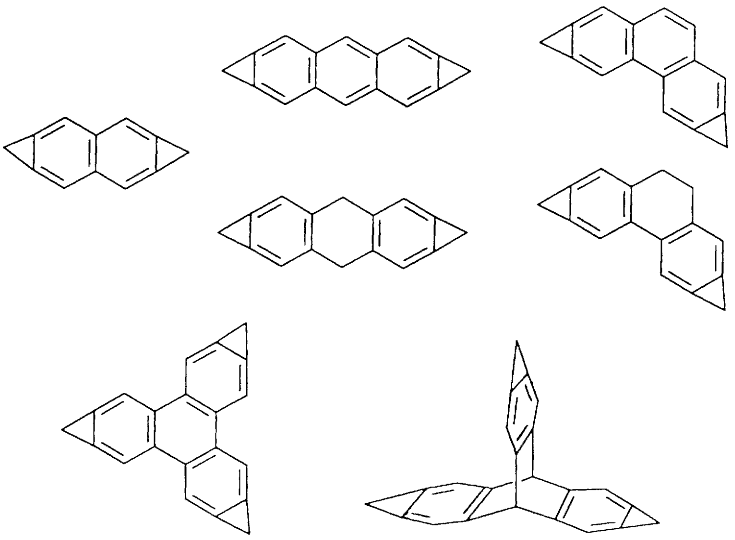
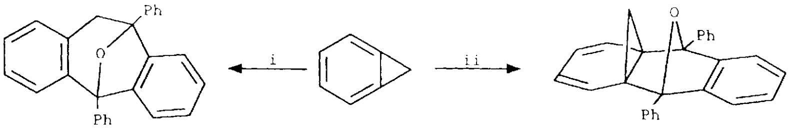
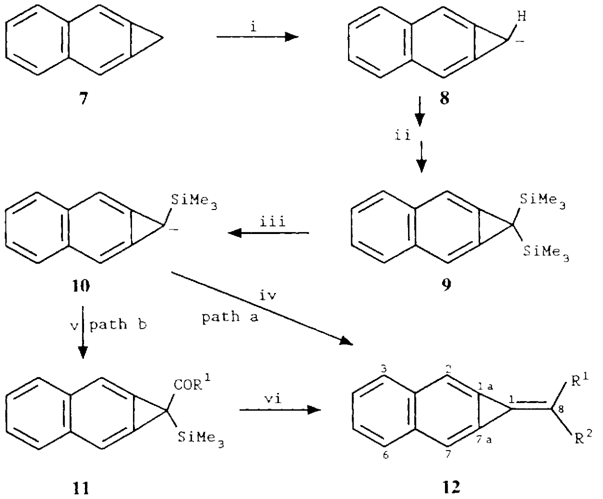


Fig. 1 Di- and tri-cycloproparenes



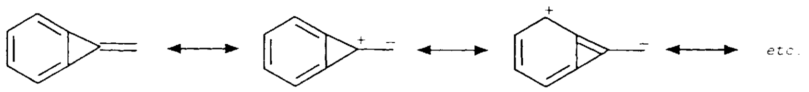
Scheme 1 *Reagents and conditions:* i, DPIBF, CHCl$_3$, room temp.; ii, DPIBF, THF, room temp



Scheme 2 *Reagents and conditions:* i, BuLi, THF; ii, Me$_3$SiCl, BuLi, Me$_3$SiCl; iii, Bu^{t}OK, THF; iv, R^{1}R^{2}CO; v, R^{1}COX; vi, LiR^2

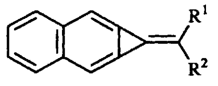
The transformation of C-1 of a cycloproparene from sp^3 to sp^2 with an attendant exocyclic double bond generates intriguing classes of compounds that combine into a single molecule the features of an *ortho*-bridged aromatic and the cross-conjugation of a triafulvene and a radialene (see Scheme 3). Cyclopropabenzenone and its derivatives are capable only of transient existence[27] although the parent has now been isolated and characterised in a matrix[28] and by low-temperature NMR in solution[29] In comparison, with an exocyclic carbon–carbon double bond a range of compounds have been prepared and characterised.[24,30–32] Theoretical studies[33] of the unknown parent **13** lead to the expectation of an enhancement in the stability of the molecule because of charge separation, and a dipole moment of 1.49 D is predicted to lie in the direction of the exocyclic carbon atom (Scheme 3). A number of the derivatives substituted at the exocyclic centre show polarities within the range 1–3.5 D. The precise magnitude is dependent upon the nature of the attached substituents and whether or not the molecule is a simple fulvene[30] or a ring annelated fulvalene.[32] Moreover, the cycloproparenyl moiety is ambiphilic as it can sustain both positive and negative charge depending upon the electron withdrawing or donating ability of the substituents attached to the exocyclic centre, *e.g.* **12b** *versus* **12c**.[30,31]

One of the more surprising features of the alkylidenecycloproparenes is their stability. Almost without exception the compounds are beautifully coloured crystalline materials that remain unchanged in the solid state for a period of years, and in solution (in the absence of electrophiles and under anaerobic conditions) for many months! In exploring this fascinating class of compounds we were astounded, but delighted, to find that the dimethylaminophenyl derivative **12d** is a notable lumophore. This compound and its analogue **12c** display[34] intense fluorescence (Y_F: **12c**, 0.81; **12d**, 0.96) that outweigh those of their cyclopropabenzene analogues. With the advantage of hindsight, it became obvious that the alkylidenecycloproparenes are formally valence bond isomers of the unknown 1,7-didehydroheptafulvenes. As such, they have a significant volume of space available for the C-8 exocyclic substituent(s), and can thus attain a conformation that is closer to planarity than can occur with their heptafulvene analogues.[35] This allows a more effective orbital overlap and enhanced conjugation (*vide infra*). Encouraged by the serendipitous discovery we have sought other exocyclically substituted alkylidenecyclopropa[*b*]naphthalenes that offer potential as new organic materials from the presence of an extended and fully delocalised π-electron system. Apart from providing the previously unpublished preparations of **12c** and **d**, we report here on the synthesis and spectroscopic properties of the conjugated 6π 5-atom heterocyclic derivatives **12e–j**, the 4- and 2-pyridylmethylidene analogues **12k** and **l**, and the sulfanyl derivative **12m**. Crystallographic data for the anilino derivatives **12c** and **d**, and the thienyl compound **12e** have been obtained and provide the first structural study of heteroatom substituted methylidenecycloproparenes.



13 $\mu_{(calc.)}$ 1.49 D

Scheme 3



12

a $R^1 = R^2 = H$
b $R^1 = R^2 = 4\text{-}O_2NC_6H_4$
c $R^1 = R^2 = 4\text{-}Me_2NC_6H_4$
d $R^1 = H, R^2 = 4\text{-}Me_2NC_6H_4$
e $R^1 = H, R^2 =$ 2-thienyl ($\mu = 2.76$ D)
f $R^1 = R^2 =$ 2-thienyl ($\mu = 9.06$ D)
g $R^1 = Ph, R^2 =$ 2-thienyl
h $R^1 = H, R^2 =$ 2-furyl
i $R^1 = H, R^2 =$ *N*-methylpyrrol-2-yl
j $R^1 = H, R^2 =$ ferrocenyl
k $R^1 = H, R^2 = 4\text{-}C_5H_4N$ ($\mu = 3.37$ D)
l $R^1 = H, R^2 = 2\text{-}C_5H_4N$
m $R^1 = Ph, R^2 = 4\text{-}C_6H_4\text{—}S\text{—}(4'\text{-}C_6H_4Me)$
n $R^1 = Me, R^2 =$ 2-thienyl
o $R^1 =$ 2-furyl, $R^2 =$ 2-furylcarbonyl

Results and discussion

The initial exploration of fulvenes derived from simple cycloproparenes was restricted to derivatives from routinely available aromatic aldehydes and ketones.[24,30–32] Similarly, easily available cyclically conjugated ketones have provided a limited range of fulvalene analogues.[32] These compounds come by way of the disilyl derivative **9** that is itself prepared from **7** (Scheme 2). The use of the disilyl compound **9** stems from the fact that all attempts to isolate the monosilyl analogue from interception of the anion **8** fails; cyclopropa[*b*]naphthalene **7** and the disilyl compound **9** are formed in essentially equimolar quantities. This differs from reactions in the cyclopropabenzene series where the monosilyl derivative is isolated[23,24] and there appears to be no simple explanation for the dichotomy. In our earlier studies[24,30–32] the silylation of **7** occupied periods of up to 8 h (prior to storage overnight) because a sequence of reagent additions and temperature manipulations was employed. We have now found that the reagent additions can be completed in 3 h by performing all of the operations at −70 °C. The yield of **9** is reduced somewhat (50–60 *versus* 66%) but the efficacy of the procedure more than offsets this, especially as the disilyl compound **9** can be stored indefinitely at ambient temperature. However, for reproducible results it is important that **7** be dried *in vacuo* over phosphorus pentoxide and stored in a desiccator prior to use.

Synthesised in this way, the stable disilyl compound **9** is easily desilylated to the monosilyl anion **10** upon reaction with *tert*-butoxide (Scheme 2).[24,30–32] Interaction of this with the relevant carbonyl compound has now provided the alkylidenecyclopropa[*b*]naphthalene derivatives **12c–m** in yields ranging from 36 to 87%. These include the 2-thienyl **12e–g**, 2-furyl **12h**, and 2-pyrrolyl **12i** compounds, and the ferrocenyl derivative **12j**, as the first examples of 6π 5-atom-substituted methylidene derivatives. The pyridyl analogues **12k**, and **l** have also been prepared and follow logically from the previously reported arylmethylidene compounds, *e.g.* **12c**,**d**. In order to extend conjugation beyond a single aromatic ring carrying an attached auxochrome, *e.g.* **12d**, the sulfide **12m** has been synthesised from 4-benzoylphenyl *p*-tolyl sulfide.[36] Attempts to obtain the thienylethylidene compound **12n** by the reaction of **10** with 2-acetylthiophene have thus far failed presumably because of competing enolate ion formation in the basic medium. The formation of the hydrocarbon **7** as the only characterisable product in *ca.* 70% yield is presumed to follow from protonation of the enolate upon work-up and desilylation of **9** under the alkaline conditions thus produced. In addition, attempts to generate a bis-alkylidene from separate reactions of **10** with each of the carbonyl groups of furil has also failed not only to provide the sought after material, but also to give even the mono-Peterson product **12o**; much decomposition is recorded. With the exception of the sulfanyl derivative **12m** (an oil) the new compounds are coloured crystalline materials. The furyl **12h** and pyrrolyl **12i** derivatives are somewhat unstable in air and room light whereas the yellow thienyl **12e** and the orange-red dithienyl **12f** compounds are crystalline and air-stable.

Each of the new methylidenecyclopropanaphthalenes reported displays spectral properties fully in accord with the assigned structure (Experimental section). In particular, 2D C–H correlation spectroscopy (COSY) and long-range heteronuclear multiple-bond connectivity (HMBC) NMR experiments have allowed for unambiguous assignment of the resonances. The ^{13}C NMR spectra show characteristic[37] shielding of the cycloproparenyl C-2 and C-7 carbons. Those of the 6π 5-atom heterocyclic derivatives **12e–j** are narrowly grouped over a 1.6 ppm range (106.4–108.0 ppm) while the pyridyl analogues **12k** and **12l** fall between 109.5 and 110.2 ppm. The C-2(7) resonances of the phenylsulfanyl derivative **12m** are fortuitously coincidental and the signal is recorded at δ 107.25. It is interesting to note that the ^{13}C NMR data for 4-pyridyl derivative **12k** fit the established $^{13}C\text{-}\sigma_{para}{}^{+}$ correlations for the range of known *para* substituted arylmethylidenecyclopropanaphthalenes[37] and an 'effective' $\sigma_{para}{}^{+}$ of *ca.* +0.95 is extracted for the 4-pyridyl moiety. In the proton spectra the influence of ring fusion is less evident and the 2-H and 7-H fall between 7.2 and 7.8 ppm as *para*-coupled doublets. The mass spectra of the compounds display intense molecular ions except for **12h** and **k**, and in the IR region the typically weak stretch from combination of the endo- and exocyclic double bonds[30] at *ca.* 1760 cm^{-1} is recorded for all of the compounds. The sulfide **12m** shows no unusual behaviour and is not discussed further.

The presence of polarity within the methylidenecycloproparenes has already been demonstrated[30–32] and from the range of new compounds reported herein three compounds were selected for capacitance and refractive index measurement to give the respective dielectric constant and, ultimately, the permanent dipole moment.[38] The values for **12e**,**f** and **k** are 2.76, 9.06 and 3.37 D, respectively. The magnitudes displayed by the mono-substituted methylidene compounds **12e** and **k** are higher than that recorded previously for **12d** (1.8 D) and the value for the dithienyl compound **12f** is markedly higher than of **12c** (3.0 D).[30]

While many of the new compounds luminesce in room light, the pyrrolyl derivative **12i**, like its anilino analogue **12d**, is by far the most notable. Fluorescence measurements have been recorded for the 6π 5-atom derivatives **12e**,**f**,**h**,**i** and **j**

(Experimental section). The ferrocenyl compound **12j** shows no significant fluorescence but its electronic absorption spectra display the same negative solvatochromy as the other compounds, *viz.* a shift of the absorption maxima to lower wavelength by *ca.* 4 nm in changing the solvent from cyclohexane to acetonitrile. The furan **12h** has modest fluorescence whereas the thienyl analogues **12e** and **f** show only weak emissions that are diminished in acetonitrile; the solvatochromic effects parallel those for the absorption spectra. In contrast to these compounds, the pyrrolyl derivative **12i** displays exceptionally intense fluorescence and, while we are unable to measure Y_F, the relative intensities indicate an efficiency ~90%. None of the Stokes shifts are exceptional. Thus, of the methylidene compounds **12** so far synthesised it is the *N,N*-dimethylanilines **12c,d** and the *N*-methylpyrrole **12i** that exhibit the most intense fluorescence. As **12i** is air/light sensitive it is more than interesting to note that the discovery of the most active and stable compound, namely **12d**, was serendipitous! Any possible disappointment with the luminescence qualities of the thiophenes **12e** and **f** and the ferrocene derivative **12j** must be offset against the current interest that they must engender for examination as non-linear optical materials as judged by the range of highly conjugated ferrocenes and thiophenes that have been assessed.[39]

X-Ray crystal structures of the methylidenecyclopropa[*b*]naphthalenes 12c–e

Of the range of cycloproparenes carrying a C-1 exocyclic olefin only one compound, namely 1,1-diphenylmethylidene-1*H*-cyclopropabenzene, has had its structure confirmed by X-ray crystallographic analysis.[24] Notwithstanding this, a discussion of the structures of **12c** and **d** has appeared in review form,[40] but the data have been neither presented nor deposited. Of the range of compounds now available, suitable single crystals of **12c–e** are available and an investigation of the structural features of the methylidenecyclopropanaphthalenes carrying electron-rich ring systems has been undertaken.

The crystal structures of **12c–e** each consist of well separated molecules. There are no significant H ··· H intermolecular contacts (**12c**: H(9) ··· H(28), 2.31; **12d**: H(6) ··· H(19), 2.22; **12e**: H(4) ··· H(12), 2.51 Å, respectively) and the shortest N ··· H contacts in **12c** and **d** are H(9) ··· N(2) (2.54 Å) and H(2) ··· N(1) (2.597 Å), respectively; thienyl **12e** has no notable S ··· H contacts. As depicted in Figs. 2–4 compounds **12c–e** are confirmed as the requisite methylidene derivatives and relevant bond lengths and interbond angles are listed in Tables 1–3. In each case the cyclopropanaphthalene moiety adopts an almost planar arrangement with the three-membered ring displaced from the plane by only 2–3° [see Fig. 4(*b*)] as is typical for the cycloproparenes.[2,40] The mono(dimethylaminophenyl) and the thienyl derivatives **12d** and **e** have the pendant 6π C_6 and 6π C_4S aromatic rings, respectively, close to planarity with the cycloproparenyl system (twist angles are *ca.* 5°) while for the diaryl compound **12c** the substituted phenyl rings are rotated out of plane by 28.2 and 27.7°. These values are markedly *less* than the values of 37–45° recorded for comparably substituted hepta-[35,41] and penta-fulvenes[42] but are akin to the values determined for a range of (*E*)-stilbenes.[43] Thus the twist angles of *ca.* 5° recorded for **12d** and **e** match those for the phenyl rings in (*E*)-stilbene itself, while those of **12d** compare well with *o,o'*-dimethyl-substituted (*E*)-stilbenes (*ca.* 25°) and not the values of 45–50° between the substituents recorded for 1-chloro-1,2,2-triphenylethene.[43b] The present data are consistent with alkylidenecycloproparenes having the exocyclic substituents twisted out-of-plane to an extent that is not large enough to prevent conjugation throughout the molecule as occurs for many other fulvenes. Thus electron delocalisation and charge separation are likely to involve mesomerism and *not* polarisation of the exocyclic carbon atom by C-1' as has been implied in the fulvene series.[35,44]

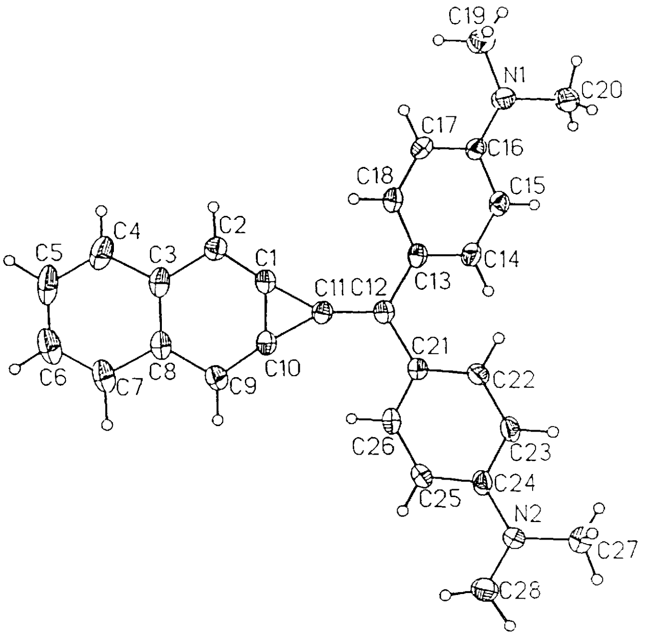


Fig. 2 X-Ray crystal structure of compound **12c** with the crystallographic labelling of the atoms

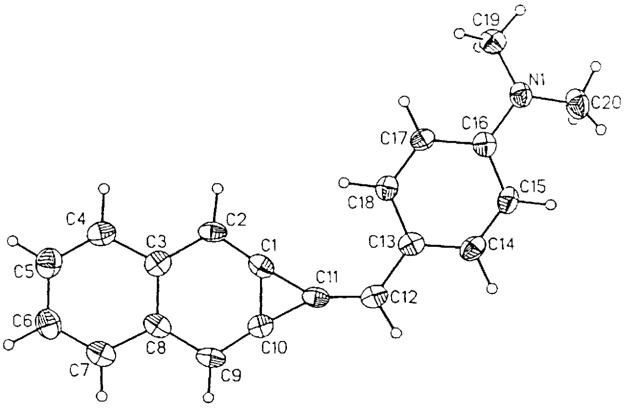


Fig. 3 X-Ray structure of compound **12d** with the crystallographic labelling of the atoms

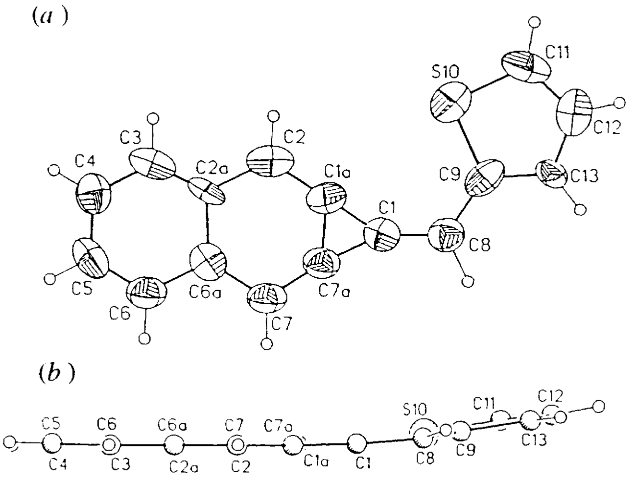


Fig. 4 X-Ray structure of compound **12e** (*a*) with the systematic labelling of the atoms, and (*b*) showing the near planarity of the molecule

Table 1 Selected bond lengths, interbond angles and torsion angles for compound **12c**

Bond lengths	(Å)	Interbond angles	(°)
N(1)–C(16)	1.387 (3)	C(2)–C(1)–C(10)	124.2 (2)
N(2)–C(24)	1.379 (3)	C(1)–C(1)–C(11)	174.8 (2)
C(1)–C(2)	1.349 (4)	C(10)–C(1)–C(11)	60.6 (2)
C(1)–C(10)	1.399 (3)	C(1)–C(2)–C(3)	114.4 (2)
C(1)–C(11)	1.445 (3)	C(2)–C(3)–C(8)	121.0 (2)
C(2)–C(3)	1.445 (3)	C(3)–C(8)–C(9)	121.6 (2)
C(3)–C(4)	1.412 (4)	C(8)–C(9)–C(10)	114.3 (2)
C(3)–C(8)	1.431 (4)	C(1)–C(10)–C(9)	124.4 (2)
C(4)–C(5)	1.375 (4)	C(1)–C(10)–C(11)	61.3 (2)
C(5)–C(6)	1.391 (5)	C(9)–C(10)–C(11)	174.1 (3)
C(6)–C(7)	1.358 (5)	C(1)–C(11)–C(10)	58.1 (2)
C(7)–C(8)	1.425 (3)	C(1)–C(11)–C(12)	150.9 (2)
C(8)–C(9)	1.429 (4)	C(10)–C(11)–C(12)	151.0 (2)
C(9)–C(10)	1.355 (3)	C(11)–C(12)–C(13)	120.0 (2)
C(10)–C(11)	1.436 (3)	C(11)–C(12)–C(21)	119.0 (2)
C(11)–C(12)	1.346 (3)	C(13)–C(12)–C(21)	120.9 (2)
C(12)–C(13)	1.477 (3)		
C(12)–C(21)	1.477 (3)		

Torsion angles	(°)
C(1)–C(11)–C(12)–C(13)	−3.5
C(1)–C(11)–C(12)–C(21)	179.9
C(11)–C(12)–C(13)–C(14)	−146.9
C(11)–C(12)–C(13)–C(18)	27.8
C(11)–C(12)–C(21)–C(22)	−150.2
C(11)–C(12)–C(21)–C(26)	27.7
C(13)–C(12)–C(21)–C(22)	33.2

Table 2 Selected bond lengths, interbond angles and torsion angles for compound **12d**

Bond lengths	(Å)	Interbond angles	(°)
N(1)–C(16)	1.398 (2)	C(2)–C(1)–C(10)	124.6(2)
C(1)–C(2)	1.346 (3)	C(2)–C(1)–C(11)	174.4(2)
C(1)–C(10)	1.395 (3)	C(10)–C(1)–C(11)	61.0(1)
C(1)–C(11)	1.448 (3)	C(1)–C(2)–C(3)	114.6(2)
C(2)–C(3)	1.433 (3)	C(2)–C(3)–C(8)	120.9(2)
C(3)–C(4)	1.417 (3)	C(3)–C(8)–C(9)	121.6(2)
C(3)–C(8)	1.440 (3)	C(8)–C(9)–C(10)	114.8(2)
C(4)–C(5)	1.365 (3)	C(1)–C(10)–C(9)	123.9(2)
C(5)–C(6)	1.410 (3)	C(1)–C(10)–C(11)	61.3(1)
C(6)–C(7)	1.365 (3)	C(9)–C(10)–C(11)	174.8(2)
C(7)–C(8)	1.415 (3)	C(1)–C(11)–C(10)	57.7(1)
C(8)–C(9)	1.425 (3)	C(1)–C(11)–C(12)	149.5(2)
C(9)–C(10)	1.354 (3)	C(10)–C(11)–C(12)	152.8(2)
C(10)–C(11)	1.443 (3)	C(11)–C(12)–C(13)	125.1(2)
C(11)–C(12)	1.329 (3)		
C(12)–C(13)	1.455 (3)		

Torsion angles	(°)
C(1)–C(11)–C(12)–C(13)	−2.0
C(10)–C(11)–C(12)–C(13)	176.8
C(11)–C(12)–C(13)–C(14)	−176.9
C(11)–C(12)–C(13)–C(18)	0.4
H(12)–C(12)–C(13)–C(14)	1.7
H(12)–C(12)–C(13)–C(18)	179

Table 3 Selected bond lengths, interbond angles and torsion angles for compound **12e**

Bond lengths	(Å)	Interbond angles	(°)
C(1)–C(1A)	1.403 (11)	C(1A)–C(1)–C(7A)	58.7 (6)
C(1)–C(7A)	1.415 (12)	C(1A)–C(1)–C(8)	146.7 (8)
C(1)–C(8)	1.351 (12)	C(7A)–C(1)–C(8)	154.3 (8)
C(1A)–C(2)	1.400 (12)	C(1)–C(1A)–C(2)	178.6 (9)
C(1A)–C(7A)	1.381 (11)	C(1)–C(1A)–C(7A)	61.1 (6)
C(2)–C(2A)	1.462 (12)	C(2)–C(1A)–C(7A)	119.0 (8)
C(2A)–C(3)	1.245 (12)	C(1A)–C(2)–C(2A)	120.8 (8)
C(2A)–C(6A)	1.498 (11)	C(2)–C(2A)–C(6A)	114.4 (7)
C(3)–C(4)	1.371 (13)	C(2A)–C(6A)–C(7)	123.1 (7)
C(4)–C(5)	1.358 (14)	C(6A)–C(7)–C(7A)	114.9 (7)
C(5)–C(6)	1.354 (12)	C(1)–C(7A)–C(1A)	60.2 (6)
C(6)–C(6A)	1.412 (12)	C(1)–C(7A)–C(7)	171.7 (9)
C(6A)–C(7)	1.431 (11)	C(1A)–C(7A)–C(7)	127.7 (7)
C(7)–C(7A)	1.348 (12)	C(1)–C(8)–C(9)	122.8 (7)
C(8)–C(9)	1.440 (12)	C(8)–C(9)–S(10)	123.2 (6)
C(9)–S(10)	1.740 (8)	C(9)–S(10)–C(11)	91.7 (4)

Torsion angles	(°)
C(1A)–C(1)–C(8)–C(9)	−2.5
C(7A)–C(1)–C(8)–C(9)	−170.9
C(1)–C(8)–C(9)–S(10)	−2.7
C(1)–C(8)–C(9)–C(13)	175.6

The impact of incorporating a double bond at C-1 of cyclopropa[*b*]naphthalene **7** upon the cycloproparenyl moiety has been discussed for **12c** and **d**. The discussion is not repeated here save to note that the C(1a)–C(7a) bridge bonds are *lengthened* in comparison to parent **7**[6,16a] and the sum of the interatomic distances in the naphthalene moieties are *shorter* than in cyclopropanaphthalene **7**. The data are consistent with mesomeric electron donation from the dimethylamino group(s). Moreover, the deviation from planarity of the nitrogen atoms of **12c** (at distances of 0.229 and 0.119 Å from the surrounding atoms) and **d** (0.283 Å), the short N–C$_{ipso}$ bonds [**12c**: 1.387(3) and 1.379(3); **12d**: 1.398(2) Å] and the difference in the mean bond differences of *e.g.* C(13)–C(14/18) and C(16)–C(15/17) to C(14)–C(15) and C(17)–C(18), support the assumption that the dipoles in these molecules (**12c**: 3.0; **12d**: 1.8 D) have the cycloproparenyl moiety as the electron acceptor. The data concerning the mean bond difference referred to for **12c** correlate very well with a linear regression found for the same atoms in 106 structure determinations of *N*,*N*-dimethylaminophenyl derivatives in the Cambridge Crystallographic Data File.[45]

Because of lower crystal quality the structural data for the thienyl derivative **12e** have less accuracy (R: 0.0712; R_w: 0.0786) than those for **12c** and **d**, and while the thienyl moiety is the presumed electron donor (μ 2.76 D) the bond lengths recorded do not allow for the same summation comparisons. The important feature recorded here is the demonstration of a near planar molecule as discussed above.

Conclusions

The cycloproparenes are easily transformed into a range of C-1 methylidene derivatives that may carry simple aromatic and heteroaromatic substituents. Such compounds mono-substituted at the exocyclic (C-8) centre are likely to be almost planar as demonstrated by the structural data of **12d** and **e**. Diaryl-substituted analogues display a twisting of the rings about the C(8)–C$_{ipso}$ bonds to an extent of only *ca.* 30° when the *ortho* positions are unsubstituted. The compounds are polar and many fluoresce. In our view mesomeric donation throughout the molecular frame best explains the results without the need to advance polarisation concepts. The thienyl **12e–h** and the ferrocenyl **12j** derivatives offer potential in the field of non-linear optics.

Experimental

Melting points were determined using a Reichert Thermovar hot-stage melting point apparatus and are uncorrected. Microanalyses were performed by the microanalytical facility of the University of Otago, Dunedin, New Zealand. Low-resolution mass spectra were recorded at 70 eV on a Hewlett-Packard 5995, and accurate mass data were from a Kratos MS80 RFA instrument. IR spectra were recorded for KBr disks on a BIORAD FTS-7, UV–VIS spectra on a Hewlett Packard 8452A Diode Array Spectrophotometer and fluorescence spectra on a Perkin-Elmer LS50B luminescence spectrometer. ^1H and ^{13}C NMR spectra were recorded on either a Varian Associates FT80A or a Bruker AC 300E instrument at 79.56 and 20.00, and 300 and 75 MHz, respectively, in [^2H]chloroform solutions with tetramethylsilane as internal standard; *J* values are given in Hz. Merck silica gel grade 60, 230–400 mesh, 60 Å was used for flash column chromatography. DC-Alufolien Kieselgel 60 F254 (layer thickness: 0.2 mm) was used for all TLC analyses. Solvents were purified using procedures in Perrin, Armarego and Perrin.[46] The concentration of butyllithium was checked by the method of Winkle, Lansinger and Ronald.[47] Tetrahydrofuran (THF) was distilled from potassium/benzophenone immediately before use. Potassium *tert*-butoxide was sublimed before use using a Büchi GKR-51 ball oven in sublimation mode. Dipole moments were determined for AnalaR grade benzene solutions (0.05–0.10 mol dm^{-3}) by the method of Guggenheim and Smith[38] using a small ~2 cm^3 variable capacitance cell with analytically pure (C,H) compounds. Impedance readings were taken with the cell open and closed employing a Hewlett Packard 913 vector impedance meter operating at 1.0 MHz. The recordings were taken at ambient temperature. Refractive index measurements were made on an Abbe 60 Refractometer. The following compounds were used as standards and their dipole moments (in Debye units) were recorded several times during the study: diphenyl sulfone μ = 5.08 (19 °C) [lit.,[48] 4.98 (20 °C)], phenyl benzoate μ = 1.87 (20 °C) [lit.,[48] 1.86 (22 °C)]. 1-[(4-methoxyphenyl)methylidene]-1*H*-cyclopropa[*b*]naphthalene μ = 1.45 (20 °C) [lit.,[32] 1.4 (22 °C)].

2-Acetylthiophene

The title compound was prepared from thiophene (21.0 g, 0.25 mol), acetic anhydride (12.75 g, 0.125 mol) and phosphoric acid (85%; 1 cm^3) according to the literature[49] as a pale yellow liquid (10.5 g, 66%) (lit.,[49] 70%). The ^1H NMR data were in agreement with those reported.[50]

Phenyl 2-thienyl ketone

The title compound was prepared from thiophene (10 g, 0.12 mol), benzoyl chloride (17.5 g, 0.125 mol) and aluminium chloride (16.7 g, 0.125 mol), according to the literature[51] as pale brown needles (light petroleum) (13.42 g, 60%), mp 52–53 °C (lit.,[51] 68%, mp 55–56 °C).

Di-2-thienyl ketone

The title compound was prepared from thiophene-2-carboxylic acid (5 g, 39 mmol), thiophene (3.45 g, 40 mmol) and phosphorus pentoxide (6.6 g) according to the literature[52] as white needles (4.70 g, 62%), mp 86–87 °C (lit.,[52] 66%, mp. 88–89 °C).

1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene 9

To a solution of 1*H*-cyclopropa[*b*]naphthalene[53] **7** (4.00 g, 28.5 mmol) in dry THF (125 cm^3) cooled to −70 °C under nitrogen was added dropwise butyllithium in hexane (2.3 mol dm^{-3}; 28.3 mmol, 12.3 cm^3). The dark solution was stirred for 25 min after which trimethylsilyl chloride (3.6 cm^3, 28.3 mmol) was added slowly by syringe. Stirring was continued for 20 min and then butyllithium (2.3 mol dm^{-3}; 6.2 cm^3, 14.2 mmol) was added to the mixture. Stirring was continued for a further 25 min and then a second portion of trimethylsilyl chloride (1.8 cm^3, 14.2 mmol) was added as before; stirring was continued for 20 min. A third aliquot of butyllithium (2.3 mol dm^{-3}; 6.2 cm^3, 14.2 mmol) was added and, after the mixture had been stirred for 35 min, trimethylsilyl chloride (1.8 cm^3, 14.2 mmol) was added. The reaction mixture was allowed to warm to room temperature overnight with stirring, after which it was quenched ($NaHCO_3$, saturated; 75 cm^3), and the aqueous layer separated and extracted with light petroleum (2 × 75 cm^3). The combined organic layer and extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give a brown solid. Dry column chromatography (silica gel, dichloromethane–light petroleum, 1:50) gave 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene **9** (4–5 g, 50–62% as colourless prisms (light petroleum), mp 95–96 °C (lit.,[24] 66%, mp 95–96 °C).

Olefination of the disilyl compound 9

The dimethylaminomethylidene compounds **12c** and **d** were prepared according to the published method[24] but are also available from the modified procedure given below.

1-Bis(4-dimethylaminophenyl)methylidene-1*H*-cyclopropa[*b*]-naphthalene[30] 12c. Orange–red needles (dichloromethane–light petroleum, 1:2) (470 mg, 55%): mp 179–180 °C (Found: C, 86.2, H 6.8, N, 7.2. $C_{28}H_{26}N_2$ requires C, 86.0; H, 6.7; N, 7.2%); ν_{max}(KBr)/cm^{-1} 1600, 1510, 1345, 1185, 1160, 1135, 940, 815, 745 and 615; λ_{max}(cyclohexane) nm 235.5 (4.62), 271.5 (4.40), 289 (4.31), 375 (4.18), 446 (4.55) and 480 (log ε 4.72); λ_{max}(acetonitrile)/nm 235 (4.62), 273 (4.43), 291sh (4.34), 380.5 (4.15), 448sh (4.51) and 481 nm (log ε 4.71); δ_H 3.01 (s, 4 × CH_3), 6.80 (d, *J* 9.0, 4 H), 7.30 (m, 4 H) and 7.69 (m, 6 H): δ_H([$^2H_2$]-DMSO) 2.98 (s, 4 × Me), 6.38 (d, *J* 8.95, 4 H), 7.50 (m, 8 H) and 7.85 (m, 2 H); δ_C 40.5 (2 × Me_2), 104.5 (C-2/7), 107.0 (C-1), 112.2 (C-3′/3″/5′/5″), 121.8 (C-8), 126.0 (C-4/5), 127.9 (C-1a/7a), 128.3 (C-3/6), 128.7 (C-1′/1″), 129.4 (C-2′/2″/6′/6″), 138.5 (C-2a/6a) and 149.9 (C-4′/4″): *m*/*z* 391 (31), 390 (100, M), 375 (14), 302 (8) and 195 (25); μ^{30}/D (C_6H_6, 20 °C) 3.0.

1-(4-Dimethylaminophenyl)methylidene-1*H*-cyclopropa[*b*]-naphthalene[30] 12d. As orange needles (dichloromethane–light petroleum, 1:2) (510 mg, 94%): mp 141–142 °C (Found: C, 88.7; H, 6.4; N, 5.0. $C_{20}H_{17}N$ requires C, 88.5; H, 6.3; N, 5.2%); ν_{max}(KBr)/cm^{-1} 1595, 1495, 1330, 1180, 1170, 1135, 1120, 840, 800 and 735: λ_{max}(cyclohexane)/nm 232sh (4.49), 234 (4.50), 261.5 (4.22), 272 (4.22), 315 (3.88), 364sh (3.51), 401sh (4.18), 431 (4.59) and 464.5 (log ε 4.75): δ_H 3.05 (s, 2 × Me), 6.60 (s, 8-H), 6.86 (d, J_{AB} 8.9, 2 H) and 7.43–7.95 (complex m, 8 H); δ_C 40.4 (2 × Me), 106.4/106.5 (C-2/7), 108.2 (C-1), 108.4 (C-8), 112.8 (C-3′/5′), 126.2/126.4 (C-4/5), 126.6 (C-1a/7a or C-1′), 127.8 (C-2′/6′), 128.5(6)/128.6(5) (C-3/6), 138.2/138.9 (C-6a/2a), 149.9 (C-4′); *m*/*z* 272 (21), 271 (100, M), 255 (26), 228 (56), 227 (21), 226 (43), 215 (30), 135 (31), 127 (36) and 113 (71); μ^{30}/D (C_6H_6, 25 °C) 1.8.

Typical modified experimental procedure. To a stirred solution of the disilyl compound **9** (120 mg, 0.42 mmol) and thiophene-2-carbaldehyde‡ (52 mg, 0.46 mmol) in anhydrous THF (20 cm^3) under oxygen-free nitrogen and cooled to −70 °C, was added potassium *tert*-butoxide (52 mg, 0.46 mmol) in the same solvent (6 cm^3) over a 10 min period. The cryostat was switched off and the stirred yellow solution was left to warm to room temperature overnight. After this it was treated with water (15 cm^3) and extracted with dichloromethane (3 × 30 cm^3). The combined organic extracts were washed with saturated brine (100 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to afford a yellow crystalline solid, column chromatography (silica gel: dichloromethane–light petroleum, 1:1) of which gave 1-(2′-thienylmethylidene)-1*H*-cyclopropa[*b*]naphthalene **12e** (30 mg, 34%) as yellow plates (dichloromethane–light petroleum), mp 188–190 °C (Found: C, 82.0; H, 4.3; S, 13.7. $C_{16}H_{10}S$ requires C, 82.1; H, 4.1; S, 14.0%); ν_{max}(KBr)/cm^{-1} 3096, 3040, 2959, 2922, 2853, 1770, 1707, 1637, 1583, 1510, 1491, 1383, 1331, 1248, 1140, 1096, 1040, 951, 853, 822, 745, 693 and 617; λ_{max}(cyclohexane)/nm 292 (3.90), 388sh

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‡ If the carbonyl compound is base sensitive it is best slowly added *ca.* 10 min *after* the potassium *tert*-butoxide.)

(3.98), 4.10 (4.32) and 438 (log ε 4.43); λ_{max}(acetonitrile)/nm 292 (4.18), 384 (sh, 4.16), 406 (4.48) and 434 (log ε 4.56); λ^{Ex}_{max}§ (cyclohexane)/nm 291.5 (324), 408.5 (938), 441 (1000) and 469 (9); $\lambda^{441}_{max\ Em}$/nm 443.5 (176) and 479.5 (116); λ^{Ex}_{max}(acetonitrile)/nm 293.5 (690), 394 (998), 418.5 (888) and 442 (861); $\lambda^{441}_{max\ Em}$/nm 452.5 (146) and 474 (139); $\lambda^{392}_{max\ Em}$/nm 392 (5), 453 (144) and 474.5 (137); δ_H 6.80 (s, 8-H), 7.08 (dd, *J* 4.50 and 5.0, 4′-H), 7.17 (d, *J* 3.5, 3′-H), 7.28 (m, 5′-H), 7.49 (m, 4/5-H), 7.49 (d, J_{para} 1.50, 2-H or 7-H), 7.68 (d, J_{para} 1.50, 7-H or 2-H) and 7.90 (m, 3/6-H); δ_C 101.4 (C-8), 107.9/108.0 (C-2/7), 111.4 (C-1), 124.4 (C-5′), 124.7 (C-3′), 126.0/127.8 (C-1a/7a), 126.7/126.8 (C-4/5), 128.8/129.0 (C-3/6), 138.3/139.1 (C-2a/6a) and 143.6 (C-2′); *m/z* 236 (4.6), 235 (14.8), 234 (72, M), 202 (34), 189 (45) and 45 (100); μ/D (C_6H_6, 19 °C) 2.76.

1-(Di-2′-thienylmethylidene)-1*H*-cyclopropa[*b*]naphthalene 12f. Bright red needles (dichloromethane–light petroleum) (79 mg, 59%); mp 94–95 °C (Found: C, 75.7; H, 3.5. $C_{20}H_{12}S_2$ requires C, 75.9; H, 3.8%); ν_{max}/cm^{-1} 3100, 3048, 2920, 2851, 1776, 1728, 1694, 1605, 1582, 1485, 1414, 1343, 1277, 1235, 1146, 1119, 1076, 949 and 847; λ_{max}(cyclohexane)/nm 242 (4.83), 296 (4.53), 304 (4.55), 410sh (4.34), 438 (4.69) and 468 (log ε 4.75); λ_{max}(acetonitrile)/nm 240 (4.74), 298 (4.35), 406sh (4.12), 436 (4.24) and 466 (log ε 4.56); λ^{Ex}_{max}(cyclohexane)/nm 277 (469), 308 (426), 345.5 (301), 400 (560), 451 (329); 485.5 (463) and 570 (14); $\lambda^{485}_{max\ Em}$/nm 499 (131) and 522sh (94); λ^{Ex}_{max}(acetonitrile)/nm 404.8 (27), 479 (25) and 494 (21); $\lambda^{479}_{max\ Em}$/nm 493.5 (24), 514sh (16), 518sh (16) and 523sh (15); δ_H 7.15 (dd, *J* 4.50 and 5.0, 4′-H_2), 7.37 (dd, *J* 5.0 and 0.90 3′-H_2), 7.47 (m, 4/5-H), 7.57 (m, 5′-H_2), 7.58 (s, 2/7-H) and 7.88 (m, 3/6-H); δ_C 107.0 (C-2/7), 109.1(5) (C-1), 110.7 (C-8), 124.8(5) (C-3′), 125.6 (C-5′), 126.9 (C-4/5), 127.5 (C-4′), 127.7(5) (C-1a/7a), 139.0 (C-2a/6a) and 142.4 (C-2′); *m/z* 318 (12), 317 (26), 316 (100, M), 315 (48), 314 (40) and 271 (21); μ(C_6H_6, 21 °C)/D 9.06.

1-[Phenyl(2′-thienyl)methylidene]-1*H*-cyclopropa[*b*]naphthalene 12g. Bright orange needles (light petroleum) (71 mg, 52%) from radial chromatography (dichloromethane–light petroleum, 1 : 1 elution); mp 75–77 °C (Found: C, 85.0; H, 4.7. $C_{22}H_{14}S$ requires C, 85.1; H, 4.5); ν_{max}/cm^{-1} 3050, 2922, 2856, 1763, 1586, 1533, 1489, 1414, 1343, 1243, 1242, 1171, 1134, 1076, 1049, 943, 839, 754, 743 and 686; λ_{max}(cyclohexane)/nm 235 (4.67), 283 (4.36), 400sh (4.24), 426 (4.56) and 454 (log ε 4.59); λ_{max}(acetonitrile)/nm 240 (4.56), 287 (4.19), 422 (4.40) and 450 (log ε 4.45); δ_H 7.11 (dd, *J* 4.50 and 5.0, 4′-H), 7.29 (dd, *J* 4.0 and 0.85, 3′-H), 7.38 (dd, *J* 5.0 and 0.85 5′-H), 7.45 (m, 3 H), 7.47 (m, 3 H), 7.62 (d, J_{para} 1.3, 2-H or 7-H), 7.84 (m, 3/6-H) and 7.85 (m, 2 H); δ_C 107.0/107.2 (C-2/7), 111.1 (C-1), 115.0 (C-8), 124.8(5) (C-5′), 125.6 (C-3′), 126.7/126.8 (C-4/5), 127.0 (C-1a/7a), 127.4 (C-4′), 127.8 (C-12), 128.13 (C-10/14), 128.55 (C-11/13), 128.7/128.8 (C-3/6), 138.6/138.7 (C-2a/6a), 139.0 (C-9) and 144.2 (C-2′); *m/z* 312 (7), 311 (25), 310 (M), 309 (52), 308 (57) and 276 (15).

1-(2′-Furylmethylidene)-1*H*-cyclopropa[*b*]naphthalene 12h. Brown microcrystals (light petroleum–dichloromethane) (32 mg, 42%) from addition of 2-furaldehyde in THF (10 cm^3) to the anion **10**; mp 135–136 °C (Found: C, 88.1; H, 4.7. $C_{16}H_{10}O$ requires C, 88.0; H 4.6%); ν_{max}/cm^{-1} 3048, 2924, 1763, 1510, 1486, 1481, 1345, 1250, 1173, 1136, 1074, 1013, 851, 822 and 743; λ_{max}(cyclohexane)/nm 280 (4.20), 386sh (4.55), 408 (4.51) and 438 (log ε 4.61); λ_{max}(acetonitrile)/nm 282 (4.49), 384sh (4.55), 406 (4.79) and 434 nm (log ε 4.83); λ^{Ex}_{max}(cyclohexane)/nm 392sh (113), 411 (209), 440 (226) and 496 (4); $\lambda^{410}_{max\ Em}$/nm 410 (25), 456.5 (195), 469 (159) and 477 (177); λ^{Ex}_{max}(acetonitrile)/nm 408 (66), 434 (74) and 456 (38); $\lambda^{456}_{max\ Em}$/nm 456 (47); $\lambda^{434}_{max\ Em}$/nm 435 (45), 451 (74) and 476 (68); $\lambda^{408}_{max\ Em}$/nm 409 (17), 454.5 (62) and 476 (57); δ_H 6.45 (s, 8-H) 6.50 (dd, *J* 1.80 and 3.20, 3′-H or 4′-H) 6.56 (d, *J* 3.30, 3′-H or 4′-H), 7.46 (m, 3/6-H), 7.49 (m, 5′-H), 7.50 (s, 2-H or 7-H), 7.63 (s, 2-H or 7-H), 7.87 (m, 4/5-H); δ_C 96.5 (C-8), 107.3 (C-3′ or C-4′), 108.0(0)/108.0(2) (C-2/7), 111.1 (C-1), 112.1 (C-3′ or C-4′), 126.1/127.7 (C-1a/7a), 126.7(7)/126.8(3) (C-3/6), 128.8/129.0 (C-4/5), 138.6/139.2 (C-2a/6a), 142.2 (C-5′) and 154.1 (C-2′); *m/z* 219 (5), 218 (29, M), 189 (100), 163 (27) and 138 (57).

1-[2′-(*N*-Methylpyrrolyl)methylidene]-1*H*-cyclopropa[*b*]-naphthalene 12i. Orange microcrystals (dichloromethane–light petroleum, 1 : 1) (213 mg, 87%) from flash chromatography; mp 180–181.5 °C (Found: M$^+$, 231.1045. $C_{17}H_{13}N$ requires *M*, 231.1048); ν_{max}(KBr)/cm^{-1} 3021, 2928, 1760, 1584, 1553, 1526, 1474, 1439, 1415, 1372, 1316, 1244, 1172, 1138, 1059, 843, 750, 708, 592 and 521 cm^{-1}; λ_{max}(cyclohexane)/nm 296 (3.12), 348 (2.92), 404sh (3.49), 418sh (3.72), 430 (3.86), 452 (3.94) and 464 (log ε 4.00); λ_{max}(acetonitrile)/nm 270 (4.34), 298sh (4.14), 400sh (4.37), 426 (4.71), 456 (log ε 4.83); λ^{Ex}_{max}(cyclohexane)/nm 430.5 (175) and 464 (267); $\lambda^{464}_{max\ Em}$/nm 473.5 (258); $\lambda^{430}_{max\ Em}$/nm 430 (40) and 473 (116); λ^{Ex}_{max}(acetonitrile)/nm 428.5 (301) and 454.5 (411); $\lambda^{454}_{max\ Em}$/nm 455.5 (54) and 488 (392); δ_H 3.75 (s, N–CH_3), 6.27 (s, 4′-H), 6.47 (s, 8-H), 6.68/6.76 (both s, 3′-H/5′-H), 7.37 (d, *J* 1.49, 2-H or 7-H), 7.43 (m, 3/6-H), 7.48 (d, *J* 1.49, 7-H or 2-H) and 7.43 (m, 4/5-H); δ_C 34.2 (CH_3), 97.1 (C-8), 106.5/106.6 (C-2/7), 108.0 (C-3′ or C-4′), 108.8 (C-1), 108.9 (C-3′ or C-4′), 123.7 (C-5′), 126.3/126.5 (C-4/5), 126.7/128.0 (C-1a/7a), 128.5/128.7 (C-3/6), 132.3 (C-2′) and 138.2/138.8 (C-2a/6a); *m/z* 232 (16), 231 (100, M), 230 (45), 229 (18), 216 (26), 202 (16) and 189 (19).

1-(Ferrocenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene 12j. Lustrous brown needles (dichloromethane–light petroleum) (93 mg, 66%); mp 159–160 °C (Found: C, 78.3; H, 4.8. $C_{22}H_{16}Fe$ requires C, 78.6; H, 4.8); ν_{max}/cm^{-1} 3090, 3032, 2924, 2853, 1744, 1686, 1638, 1589, 1514, 1427, 1350, 1252, 1177, 1142, 1101, 1024, 999, 949, 928, 853, 806, 743 and 480; λ_{max}(cyclohexane)/nm 234 (4.80), 280 (4.45), 294 (4.48), 382 (4.64), 404 (4.77) and 512 (log ε 5.10); λ_{max}(acetonitrile)/nm 234 (4.57), 276 (4.19), 294 (4.22), 378 (4.46), 400 (4.52) and 512 (log ε 3.85); λ^{Ex}_{max}(cyclohexane)/nm 283 (1) and 309 (15); $\lambda^{309}_{max\ Em}$/nm 310 (30) and 340.5 (3); $\lambda^{283}_{max\ Em}$/nm 284 (16) and 309 (3); λ^{Ex}_{max}(acetonitrile)/nm 253.5 (23); $\lambda^{253}_{max\ Em}$/nm 254 (14), 310.5 (2) and 444 (2); δ_H 4.13 (s, 5 H), 4.36 (dd, *J* both 1.80, 2 H), 4.72 (dd, *J* both 1.80, 2 H), 6.31 (s, 8-H), 7.41 (d, *J* 3.0, 2-H or 7-H) 7.44 (m, 4/5-H), 7.57 (d, *J* 3.0, 2-H or 7-H) and 7.87 (m, 3/6-H); δ_C 67.2, 69.1(5), 69.6, 83.8 (C-8a), 106.4/106.5 (C-2/7), 106.9 (C-8), 109.3 (C-1), 126.3(6)/126.4(3) (C-4/5), 127.0/128.3 (C-1a/7a), 128.6(2)/128.6(5) (C-3/6), 138.0(5)/138.6 (C-2a/6a); *m/z* 338 (4), 337 (27), 336 (100, M), 278 (32) and 215 (27).

1-(4′-Pyridylmethylidene)-1*H*-cyclopropa[*b*]naphthalene 12k. Pale yellow microcrystals (95 mg, 39%) from flash chromatography (ethyl acetate–light petroleum, 3 : 1; and crystallisation from the same solvent); mp 182.5–183.5 °C (Found: C, 88.7; H, 4.7; N, 6.3. $C_{17}H_{11}N$ requires C, 89.0; H, 4.8; N, 6.1%); ν_{max}/cm^{-1} 3434, 3065, 3021, 2922, 2853, 1765, 1746, 1589, 1557, 1433, 1348, 1252, 1173, 1142, 988, 858, 841, 758 and 546; λ_{max}(cyclohexane)/nm 282 (4.19) 334 (3.42), 352sh (3.70), 352sh (3.70), 372sh (4.03), 390 (4.30) and 418 (log ε 4.40); λ_{max}(acetonitrile)/nm 284 (4.19), 332 (3.56), 372sh (4.30), 390 (4.52) and 414 (log ε 4.56); δ_H 6.44 (s, 8-H), 7.54 (m, 4/5-H), 7.54 (d, *J* 5.8 2′-H/6′-H), 7.70 (d, *J* 1.5, 2-H or 7-H), 7.82 (d, *J* 1.5, 2-H or 7-H), 7.96 (m, 3/6-H) and 8.59 (d, *J* 5.8, 3′-H/5′-H); δ_C 103.3 (C-8), 109.8/110.2 (C-2/7), 116.0 (C-1), 120.4 (C-2′/6′), 124.7/127.0 (C-1a/7a), 127.3(8)/127.4(3) (C-4/5), 129.1/129.2 (C-3/6), 138.9/139.5 (C-2a/6a), 145.3 (C-1′) and 149.9 (C-3′/5′);

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§ For all fluorescence measurements: Ex = excitation wavelength, Em = emission from specified irradiation. The numbers in parentheses are relative intensities.

m/z 230 (18), 229, (100, M), 228 (35), 227 (19), 200 (29), 175 (12) and 150 (14); μ(C_6H_6, 21 °C)/D 3.37.

1-(2′-Pyridylmethylidene)-1*H*-cyclopropa[*b*]naphthalene 12l. Flash chromatography (ethyl acetate–light petroleum, 2:1; and crystallization from the same solvent) provided pale yellow microcrystals (54 mg, 50%); mp 129–131 °C (Found: C, 88.4; H, 4.9; N, 6.0. $C_{17}H_{11}N$ requires C, 89.0; H, 4.8; N, 6.1%); ν_{max}/cm^{-1} 3549, 3478, 3414, 3240, 3057, 2924, 2853, 1765, 1638, 1618, 1584, 1510, 1464, 1429, 1138, 855 and 750; λ_{max}(cyclohexane)/nm 278 (4.11), 332 (3.47), 350sh (3.75), 378sh (4.16), 394 (4.39) and 418 (log ε 4.43); λ_{max}(acetonitrile)/nm 278 (4.34), 328 (3.72), 350sh (4.01), 370sh (4.35), 392 (4.60) and 416 (log ε 4.60); δ_H 6.75 (s, 8-H), 7.11 (m, 5′-H), 7.52 (m, 4/5-H), 7.69 (d, *J* 1.5, 2-H or 7-H), 7.73 (m, 4′-H), 7.81 (d, *J* 1.5, 2-H or 7-H), 7.94 (m, 3-H/6-H), 7.99 (d, *J* 8.24, 3′-H) and 8.62 (d, *J* 4.56, 6′-H); δ_C 107.1 (C-8), 109.5/109.8 (C-2/7), 115.1 (C-1), 120.2 (C-3′), 120.9 (C-5′), 125.4/127.3 (C-4/5), 129.1/129.2 (C-3/6), 136.1 (C-4′), 138.8/139.4 (C-2a/6a), 149.8 (C-6′) and 157.1 (C-2′); m/z 230 (16), 229 (95, M), 228 (100), 227 (24), 200 (12), 150 (10) and 114 (17).

1-{Phenyl[4′-(4″-methylphenylsulfanyl)phenyl]methylidene}-1*H*-cyclopropa[*b*]naphthalene 12m. From the disilyl compound **9** (80 mg, 0.28 mmol) and 4-benzoylphenyl 4-methylphenyl sulfide[36] **12** (99 mg, 0.32 mmol) and column chromatography (dichloromethane–light petroleum, 1:1) followed by radical chromatography as a bright orange oil (76 mg, 63%) (Found: M$^+$, m/z 426.1442. $C_{31}H_{22}{}^{32}S$ requires *M*, 426.1442); ν_{max}/cm^{-1} 3048, 2963, 2853, 1773, 1638, 1618, 1553, 1489, 1420, 1344, 1262, 1175, 1136, 1084, 1013, 845, 805, 743, 694 and 617; λ_{max}(cyclohexane)/nm 288 (4.82), 424 (4.99) and 450 (log ε 5.10); λ_{max}(acetonitrile)/nm 286 (4.23), 420 (4.34) and 442 (log ε 4.38); δ_H 2.36 (s, CH_3), 7.38 (m, 9 H), 7.34 (m, 3/6-H), 7.61 (m, 4/5-H), 7.52 (s, 2/7-H), 7.68 (m, 2 H) and 7.86 (m, 2 H); δ_C 21.9(5) (CH_3), 107.2(5) (C-2/7), 111.9 (C-8), 119.2 (C-1), 125.1, 126.8, 127.0, 127.2/127.4 (C-1a/7a), 128.2/128.5 (C-3/6), 128.6, 128.8, 129.4, 130.2, 131.0, 132.7, 136.3(5), 137.8(5), 138.8(0)/138.8(5) (C-2a/6a) and 139.3; m/z 427 (15), 426, (45, M), 302 (31) and 44 (100).

Attempted synthesis of 1-(2′-thienylethylidene)-1*H*-cyclopropa[*b*]naphthalene 12n

(i) The disilyl compound **9** (120 mg, 0.42 mmol) and 2-acetylthiophene (63 mg, 0.50 mmol) were mixed in dry THF (20 cm^3) at −70 °C after which the reaction procedure and work-up were performed as described above for compound **12c**. Column chromatography (dichloromethane–light petroleum, 1:1) gave cyclopropa[*b*]naphthalene **7** (40 mg, 68%) as the major product, mp and mixed mp 86–87 °C.

(ii) To the anion generated from the disilyl compound **9** (120 mg, 0.42 mmol) in dry THF (20 cm^3) at −70 °C was added 2-acetylthiophene (52 mg, 0.42 mmol) in the same solvent (10 cm^3) slowly over 30 min. The reaction mixture was stirred at −40 °C for 4 h and then worked up as above to provide cyclopropa[*b*]naphthalene **7** (43 mg, 73%) identical with the sample from (i) above.

Single-crystal X-ray diffraction analyses

1-[Bis(4′-dimethylaminophenyl)]methylidene-1*H*-cyclopropa[*b*]naphthalene 12c. *Crystal data.*—$C_{28}H_{26}N_2$, *M* 392.6. Orthorhombic $a = 29.993(8)$, $b = 11.514(4)$, $c = 6.404(2)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 2\,137(1)$ Å^3 (by least squares refinement on diffractometer angles for 35 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $Pna2_1$ (No. 33), $Z = 4$, $D_x = 1.210$ g cm^{-3}. Rust red needles; crystal dimensions 0.28 × 0.21 × 0.11 mm^3, μ(Mo-Kα) = 0.07 mm^{-1}.

Data collection and processing.[40]—Nicolet R3m/V diffractometer, ω scan technique with $2\theta_{max} = 45°$, graphite monochromated Mo-Kα radiation, data collection at 125 K; 2408 unique reflections (no absorption correction was performed) giving 2250 with $F_o \geqslant 4\sigma(F)$

Structure analysis and refinement.—Direct methods with full matrix least-squares refinement with SHELXTL-Plus (MicroVax Version 3.43) using the implemented atomic scattering factors. All non-hydrogen atoms were given anisotropic and hydrogen atoms isotropic temperature parameters and refined (Tables 4 and 5—Supplementary Material), the latter as rigid groups with common temperature parameters for each methyl group. The weighting scheme $\omega = 1/[\sigma^2(F_o) + 0.004{*}F_o{}^2]$ gave satisfactory agreement analyses. Final *R* and R_w values are 0.029 and 0.032.

1-(4-Dimethylaminophenyl)methylidene-1*H*-cyclopropa[b]-naphthalene 12d. *Crystal data.*—$C_{20}H_{17}N$, *M* 271.3. Orthorhombic $a = 6.274(1)$, $b = 7.469(1)$, $c = 30.945(4)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 1\,450.3(2)$ Å^3 (by least squares refinement on diffractometer angles for 50 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_12_12_1$ (No. 19), $Z = 4$, $D_x = 1.243$ g cm^{-3}. Orange needles; crystal dimensions 0.51 × 0.43 × 0.06 mm^3, μ(Mo-Kα) = 0.07 mm^{-1}.

Data collection and processing.[40]—Nicolet R3m/V diffractometer, Wyckoff scan mode with $2\theta_{max} = 50°$, graphite monochromated Mo-Kα radiation, data collection at 120 K; 2588 unique reflections (no absorption correction was performed) giving 2336 with $F_o \geqslant 4\sigma(F)$.

Structure analysis and refinement.—Direct methods with full matrix least-squares refinement with SHELXTL-Plus (MicroVax Version 3.43) using the implemented atomic scattering factors. All non-hydrogen atoms were given anisotropic and hydrogen atoms isotropic temperature parameters without further constraints. The weighting scheme $\omega = 1/[\sigma^2(F_o) + 0.000\,91{*}F_o{}^2]$ gave satisfactory agreement analyses. Final *R* and R_w values are 0.035 and 0.039.

1-(2′-Thienyl)methylidene-1*H*-cyclopropa[*b*]naphthalene 12e. *Crystal data.*—$C_{16}H_{10}S$, *M* 234.3. Monoclinic $a = 7.719(3)$, $b = 5.898(3)$, $c = 25.586(26)$ Å, $\alpha = 90$, $\beta = 90.62$, $\gamma = 90°$, $V = 1164.8(14)$ Å^3 (by least-squares refinement on diffractometer angles for 35 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/n$ (No. 14), $Z = 4$, $D_x = 1.336$ g cm^{-3}. Yellow plates; crystal dimensions 0.26 × 0.24 × 0.02 mm^3, μ(Mo-Kα) = 0.25 mm^{-1}.

Data collection and processing.[40]—Siemens P4 four-circle diffractometer, Wyckoff scan mode with $2\theta_{max} = 40°$, graphite monochromated Mo-Kα radiation, data collection at ambient temperature; 1004 unique reflections (no absorption correction was performed) giving 739 with $F_o \geqslant 4\sigma(F)$.

Structure analysis and refinement.—Direct methods with full matrix least-squares refinement with SHELXTL-Plus (SGI IRIS Indigo) using the implemented atomic scattering factors. All non-hydrogen atoms were given anisotropic and hydrogen atoms isotropic temperature parameters without further constraints. The weighting scheme $\omega = 1/[\sigma^2(F_o) + 0.002{*}F_o{}^2]$ gave satisfactory agreement analyses. Final *R* and R_w values are 0.0712 and 0.0786.

Atomic coordinates, bond lengths and interbond angles and thermal parameters for each of compounds **12c–e** have been deposited with the Cambridge Crystallographic Data Centre (see Instructions for Authors, Issue No. 1).

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References

1 Previous part, M. J. Cooney, B. Halton, M. Baumgarten and L. Gherghel, *Aust. J. Chem.*, 1995, **48**, 1167.

2 B. Halton *Cycloproparenes* in The Chemistry of the Cyclopropyl Group, Pt. 3 (ed. Z. Rappoport), Wiley Interscience, Chichester, 1995, in press.

3 B. Halton, *Chem. Rev.*, 1989, **89**, 116.

4 E. Vogel, W. Grimme and S. Korte, *Tetrahedron Lett.*, 1965, 3625; W. E. Billups, A. J. Blakeney and W. Y. Chow, *Org. Synth.*, 1976, **55**, 12.

5 R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, 1964, **86**, 525.

6 W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, P. G. Werness and J. L. Wood, *J. Am. Chem. Soc.*, 1973, **95**, 7878.

7 Y. Apeloig, D. Arad, B. Halton and C. J. Randall, *J. Am. Chem. Soc.*, 1986, **108**, 4932.

8 R. Neidlein, D. Christen, V. Poignée, R. Boese, D. Bläser, A. Gieren, C. Ruiz-Pèrez and T. Hüber, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 294; R. Boese, D. Bläser, W. E. Billups, M. M. Haley, A. H. Maulitz, D. L. Mohler and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 313; D. Bläser, R. Boese, W. A. Brett, P. Rademacher, H. Schwager, A. Stanger and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 206.

9 W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 1930, 2510.

10 A. Stanger, *J. Am. Chem. Soc.*, 1991, **113**, 8277.

11 K. Baldridge and J. S. Siegel, *J. Am. Chem. Soc.*, 1992, **114**, 9583.

12 For a leading discussion see: J. S. Siegel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1721.

13 O. Mo, M. Yanez, M. Eckert-Maksic and Z. B. Maksic, *J. Org. Chem.*, 1995, **60**, 1368.

14 A. T. McNichols and P. J. Stang, *Synlett*, 1992, 971.

15 D. Davalian, P. J. Garratt, W. Koller and M. M. Mansuri, *J. Org. Chem.*, 1980, **45**, 4183.

16 (*a*) B. Halton, R. Boese, D. Bläser and Q. Lu, *Aust. J. Chem.*, 1991, **44**, 265; (*b*) J. Ippen and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 736.

17 W. E. Billups, M. M. Haley, R. C. Claussen and W. A. Rodin, *J. Am. Chem. Soc.*, 1991, **113**, 4331.

18 W. E. Billups, D. J. McCord and B. R. Maughon, *J. Am. Chem. Soc.*, 1994, **116**, 8831.

19 R. Neidlein, B. Krämer and C. Krüger, *Z. Naturforsch. Teil B.*, 1990, **45**, 1577; R. Neidlein, M. Kohl and W. Kramer, *Helv. Chim. Acta.*, 1989, **72**, 1311; I. Durucasu, N. Saraçoglu and M. Balci, *Tetrahedron Lett.*, 1991, **32**, 7097; B. Halton and S. G. G. Russell, *Aust. J. Chem.*, 1991, **44**, 555; H. Kato, S. Toda, Y. Arikawa, M. Masuzawa, M. Hashimoto, K. Ikoma, S.-Z. Wang and A. Miyasaka, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2035; S. Kagabu, K. Saito, H. Watanabe, K. Takahashi and K. Wada, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 106; S. Kagabu and T. Inoue, *Chem. Lett.*, 1989, 2181.

20 U. H. Brinker and H. Wüster, *Tetrahedron Lett.*, 1991, **32**, 593; B. Halton and S. G. G. Russell, *Aust. J. Chem.*, 1990, **43**, 2099; K. Saito, H. Ishihara and S. Kagabu, *Bull. Soc. Chem. Jpn.*, 1987, **60**, 4141; K. Saito, K. Ito, K. Takahashi and S. Kagabu, *Org. Prep. Proced. Int.*, 1991, **23**, 196.

21 B. Halton, A. D. Woolhouse, H. M. Hugel and D. P. Kelly, *J. Chem. Soc., Chem. Commun.*, 1974, 247; P. Müller and D. Rodriguez, *Helv. Chim. Acta*, 1986, **69**, 1546.

22 C. C. L. Chai, D. Christen, B. Halton, R. Neidlein and M. A. E. Starr, *Aust. J. Chem.*, 1995, **48**, 577.

23 C. Eaborn, R. Eidenschink, S. J. Harris and D. M. R. Walton, *J. Organomet. Chem.*, 1977, **124**, C27; C. Eaborn and J. G. Stamper, *J. Organomet. Chem.*, 1980, **192**, 155.

24 B. Halton, C. J. Randall, G. J. Gainsford and P. J. Stang, *J. Am. Chem. Soc.*, 1986, **108**, 5949; B. Halton and P. J. Stang, *Acc. Chem. Res.*, 1987, **20**, 443.

25 B. Halton, M. J. Cooney and H. Wong, *J. Am. Chem. Soc.*, 1994, **116**, 11574; A. T. McNichols, P. J. Stang, B. Halton and A. J. Kay, *Tetrahedron Lett.*, 1993, **34**, 3131.

26 A. T. McNichols, P. J. Stang, D. M. Addington and B. Halton, *Tetrahedron Lett.*, 1994, **35**, 437.

27 J. Adamson, D. L. Forster, T. L. Gilchrist and C. W. Rees, *J. Chem. Soc. C*, 1971, 981; M. S. Ao, E. M. Burgess, A. Schauer and E. A. Taylor, *J. Chem. Soc., Chem. Commun.*, 1969, 220.

28 J. G. G. Simon, A. Schweig, Y. Xie and H. F. I. Schaefer, *Chem. Phys. Lett.*, 1992 **200**, 631; J. G. G. Simon, N. Münzel and A. Schweig, *Chem. Phys. Lett.*, 1990, **170**, 187; J. G. Radziszewski, B. A. Hess and R. Zahradnik, *J. Am. Chem. Soc.*, 1992, **114**, 52.

29 J. G. G. Simon and A. Schweig, *Chem. Phys. Lett.*, 1993, **201**, 377.

30 B. Halton, *Pure Appl. Chem.*, 1990, **62**, 541; B. Halton, Q. Lu and P. J. Stang, *J. Chem. Soc., Chem. Commun.*, 1988, 879;

31 B. Halton, Q. Lu and P. J. Stang, *Aust. J. Chem.*, 1990, **43**, 1277.

32 B. Halton, S. J. Buckland, Q. Lu, Q. Mei and P. J. Stang, *J. Org. Chem.*, 1988, **53**, 2418; B. Halton, S. J. Buckland, Q. Mei and P. J. Stang, *Tetrahedron Lett.*, 1986, **27**, 5159.

33 Y. Apeloig, M. Karni and D. Arad in *Strain and Its Implications* (eds. A. de Meijere and S. Blechert), Reidel, Dordrecht, 1989, p. 457.

34 B. Halton, Q. Lu and W. H. Melhuish, *J. Photochem. Photobiol., A: Chem.*, 1990, **52**, 205.

35 M. Neuenschwander, 'Fulvenes' in *The Chemistry of Double Bonded Functional Groups*, Suppl. A (ed. S. Patai), Pt. 2, Wiley Interscience, Chichester, 1989, p. 1131.

36 Maybridge Chemical Co. Ltd., Tintagel, Cornwall, UK.

37 B. Halton, Q. Lu and P. J. Stang, *J. Org. Chem.*, 1990, **55**, 3056.

38 E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714; J. W. Smith, *Trans. Faraday Soc.*, 1950, **46**, 394.

39 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.

40 R. Boese, 'Structural Studies of Strained Molecules' in *Advances in Strain in Organic Chemistry* (ed. B. Halton), vol. 2, JAI Press, London, 1992, p. 191.

41 M. Hanack, K. Ritter, I. Stein and W. Hiller, *Tetrahedron Lett.*, 1986, **27**, 3357.

42 D. Rau and U. Behrens, *J. Organomet. Chem.*, 1990, **387**, 219; J. C. Gallucci, T. M. Kravetz, K. E. Green and L. A. Paquette, *J. Am. Chem. Soc.*, 1985, **107**, 6592.

43 (*a*) K. Ogawa, T. Sano, S. Yoshimura, Y. Yakeuchi and K. Toriumi, *J. Am. Chem. Soc.*, 1992, **114**, 1041; K. Ogawa, J. Harada and S. Tomoda, Mini International Symposium on Solid State Organic Chemistry (MIS^{3}OC), Ehime University, Matsuyama, Japan, Oct. 25-27, 1993, Abstract 0–9; (*b*) E. Herdweck, W. Ziche and N. Auner, *Acta Crystallogr., Sect. C*, 1994, **50**, 81.

44 P. Bonzli and M. Neuenschwander, *Helv. Chim. Acta*, 1991, **74**, 255.

45 B. Boese and T. Haumann, unpublished observations, 1990.

46 D. D. Perrin, W. L. F. Aramarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed, Pergamon Press, London, 1980.

47 M. R. Winkle, J. M. Lansinger and R. C. Ronald, *J. Chem. Soc., Chem. Commun.*, 1980, 87.

48 As listed in the Appendix to *Trans. Faraday Soc.*, 1934, 30.

49 B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th edn., Longman Scientific and Technical, London, p. 1014.

50 M. L. Martin, *Bull. Soc. Chim. Fr.*, 1968, 698.

51 W. Minnis, *Org. Synth.*, 1932, **12**, 62.

52 R. M. Acheson, R. H. MacPhee, P. G. Philpott and J. A. Barltrop, *J. Chem. Soc.*, 1956, 703.

53 W. E. Billups and W. Y. Chow, *J. Am. Chem. Soc.*, 1973, **95**, 4099; A. R. Browne and B. Halton, *Tetrahedron*, 1977, **33**, 384.

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