Synthesis, structure and stability of *E*/*Z*-isomers of novel conjugated enamines prepared from 9-arylmethyl- or 9-arylpropenyl-9*H*-carbazole with arylmethyleneanilines

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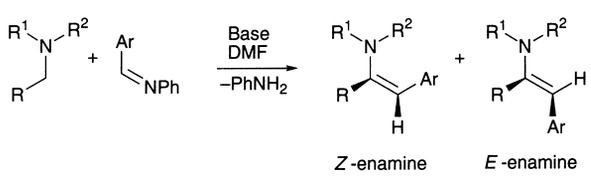
Active methylene groups, substituted by 9*H*-carbazol-9-yl (Carb) and aryl or 2-phenylethenyl groups, condense with arylmethyleneanilines in DMF at 75 °C in the presence of Bu^{t}OK to form the corresponding enamines [(Carb)(Ar^1)C=C(Ar^2)H] and dienamines [(Ar^3)HC=C(Carb)CH=CHPh] in almost quantitative yield. The ^{1}H and ^{13}C NMR spectra for the enamine 1′*Z*-isomers [16 (Ar^1 = Ar^2 = 4-fluorophenyl), 17 (Ar^1 = 4-fluorophenyl, Ar^2 = 4-*tert*-butoxyphenyl), 19 (Ar^1 = Ar^2 = 4-*tert*-butoxyphenyl)], dienamine 1′*Z*-isomers [14a (Ar^3 = 1-naphthyl), 14b (Ar^3 = 4-methoxyphenyl), 14c (Ar^3 = Ph)] and 1′*E*-isomers [15a (Ar^3 = 1-naphthyl), 15c (Ar^3 = Ph)] and precursors are assigned with the aid of COSY, HMBC, and HMQC techniques. The geometrical isomerism of the different dienamines 14–15 is established by $^3J_{C\text{-}H}$ NMR couplings and that of enamine 12 by a difference NOE experiment. X-Ray crystal structures for 16, 14a and 15c corroborate the isomerism results deduced by NMR studies. Dienamines 14a and 15a hydrolyse to the ketone under relatively strong acid conditions [AcOH–HCl–H$_2$O (18 : 1 : 1 v/v)] under reflux over 7 h. There is an equilibrium between 14c and 15c in 1,2,4-trichlorobenzene at 180 ± 1 °C with *K* = 15c/14c = 0.77 as estimated from the kinetic rate profiles from HPLC data acquired over 4 days. However, under the same conditions, 14a and 15a undergo an equilibration concurrent with a reaction (monitored over 9 days) giving apparently a carbazolyl-substituted phenylphenanthrene. In contrast, enamine 16 is thermally stable with no detectable change after boiling for 4 days in 1,2,4-trichlorobenzene.

Introduction

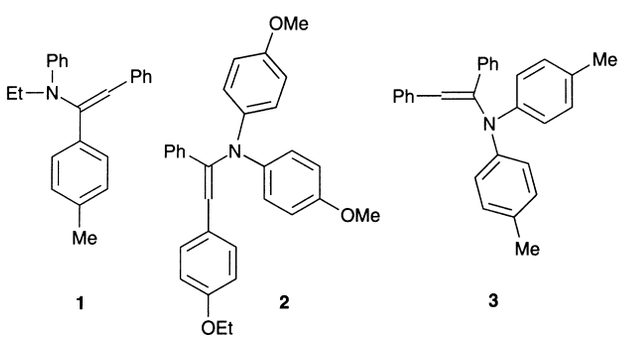
To the extensive literature on enamines,[1–3] we have recently contributed a novel, diverse method for the preparation of the aromatic-substituted enamines,[4] illustrated in Scheme 1, whose



Scheme 1

synthesis is discussed below. In addition to the synthesis, this report also presents NMR, crystallographic and other physical data on the *E*/*Z* isomerism of enamines where the more conventional amino group (R^{1}NR^2–) is replaced by a 9*H*-carbazol-9-yl moiety and the R group is either a substituted phenyl or (*E*)-cinnamoyl group. These carbazole derivatives are more amenable to isomerism studies because the enamines which form readily are more crystalline, are easier to separate, discriminate easily between the *E*- and *Z*-isomers, and hydrolyse with difficulty even when subjected to harsh conditions.

When incorporated in a polymer matrix, doped aromatic enamines **1**–**3** are useful electrophotographic photoconductors.[5] In xerography, molecules with high mobility, which is a measure of charge (or hole) transport capability when a potential is applied across a matrix containing these molecules,[6] are utilized. Compared to the analogous triaryl amines the performance measured by the mobility of the charge transport materials[7] is higher for compounds containing at least one enamine functionality (*i.e.* **5** > **4**, **7** > **6**, **9** > **8**). In conjugated systems this property should be enhanced by the electron-rich nature of these species (*cf.* mobility of **6** > **4** or **6** > **8**) and because rigid molecules may adopt a more favourable conformation when they are converted to cation radicals during the process of hole transport.[8]

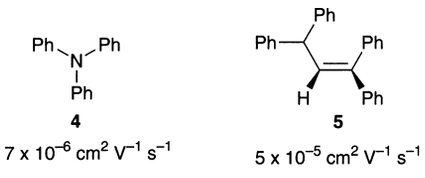


In xerographic processes,[9,10] materials containing the carbazole moiety [*e.g.* poly(vinylcarbazole)] have been utilized[10,11] due to their photoconductivity, a property which was recognized some time ago.[12] The carbazolyl-containing enamines illustrated in Schemes 2 and 3 show a greater resistance to hydrolysis compared to several reported diarylamino-containing enamines[4] (Scheme 1) which are probably of similar hydrolytic stability to **1**–**8**. On the basis of this hydrolytic stability, which is a property sought for prolonged usage,[13] and their ease of preparation and purification and good potential as hole transport materials, enamines containing the carbazolyl group should be attractive for use as photoreceptors and in similar applications.

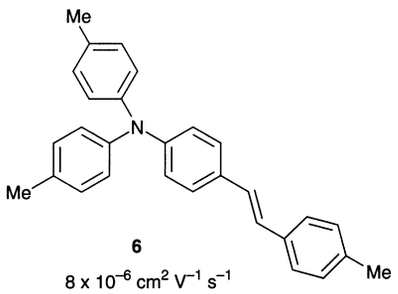
Results and discussion

Synthesis

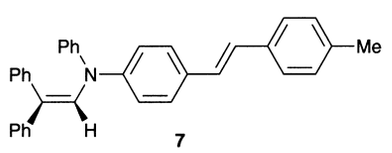
Enamines are commonly derived from the condensation of carbonyl compounds with secondary amines with the removal of water.[1b,14] This type of synthesis results in enamines which are easily hydrolysed by stirring in aqueous acid. The enamines



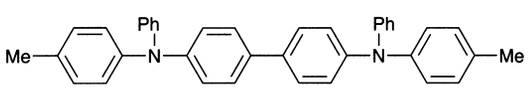
4 7×10^{-6} cm^2 V^{-1} s^{-1} **5** 5×10^{-5} cm^2 V^{-1} s^{-1}



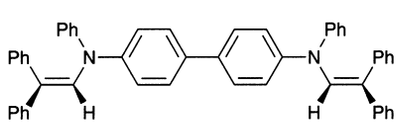
6 8×10^{-6} cm^2 V^{-1} s^{-1}



7 3×10^{-5} cm^2 V^{-1} s^{-1}



8 5×10^{-6} cm^2 V^{-1} s^{-1}



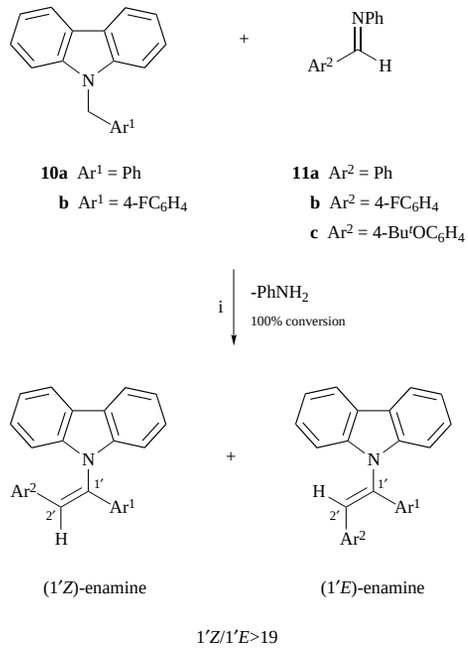
9 3.5×10^{-5} cm^2 V^{-1} s^{-1}

Values read from graphical data at $E = 12$ V μm^{-1}, $T = 295$ K and a charge-transport material to polymer binder mix of 1.76 mmol g^{-1} (ref. 8)

outlined below are not accessible by a similar condensation, probably because of the poor nucleophilicity and large steric requirements of carbazole.

Our synthesis began with an arylmethylcarbazole, easily obtained from the alkylation of carbazole with the arylmethyl chloride, followed by condensation with arylmethyleneanilines in the presence of a strong base (Scheme 2). Herein we also report some novel cross-conjugated acyclic aromatic enamines originally intended as dienes in the Diels–Alder reaction *en route* to novel polyaromatic imides (Scheme 3). These syntheses, illustrated in Schemes 2 and 3, are a variant of the anil reaction described in the numerous papers of Siegrist.[15] Siegrist has reported one example of enamine formation under similar strong basic conditions[16] but he did not realize the general applicability of this reaction. High yields of enamine[17,18] can also be obtained by starting with the benzylated amines, instead of the aryl benzyl ethers, and reacting with the imine in the presence of Bu^{t}OK (3 equiv. as also used by Siegrist[15]) as the strong base in DMF at 75 °C.

The reaction shown in Scheme 2 has been employed to prepare several enamines in good yields when there are no labile substituents present which would react in the strongly basic medium.[4] When fluorine atoms are present, the reaction proceeds as illustrated in Scheme 4. The displacement of the fluorines takes place cleanly but much more slowly than the first



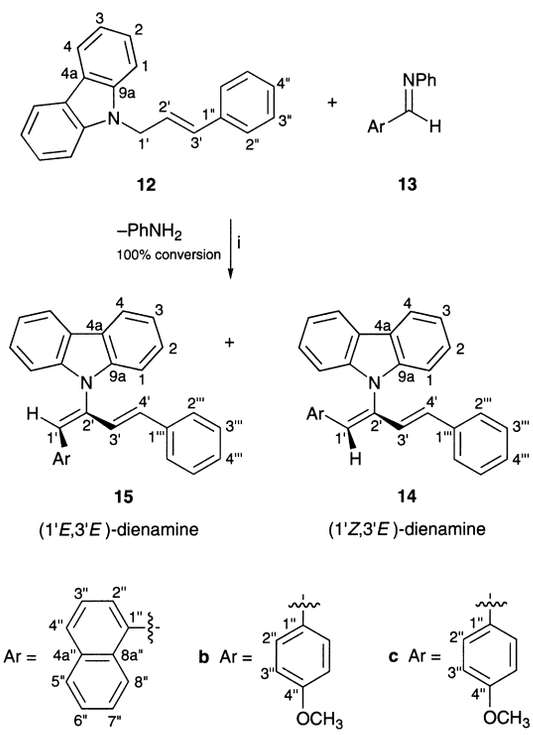
10a Ar^1 = Ph **11a** Ar^2 = Ph
b Ar^1 = 4-FC$_6$H$_4$ **b** Ar^2 = 4-FC$_6$H$_4$
c Ar^2 = 4-Bu^{t}OC$_6$H$_4$

i, -PhNH$_2$, 100% conversion

(1′*Z*)-enamine (1′*E*)-enamine

1′*Z*/1′*E*>19

Scheme 2 *Reagents and conditions:* i, DMF (50 cm^3), Bu^{t}OK (1 equiv.), 75 °C, <3 min



12 **13**

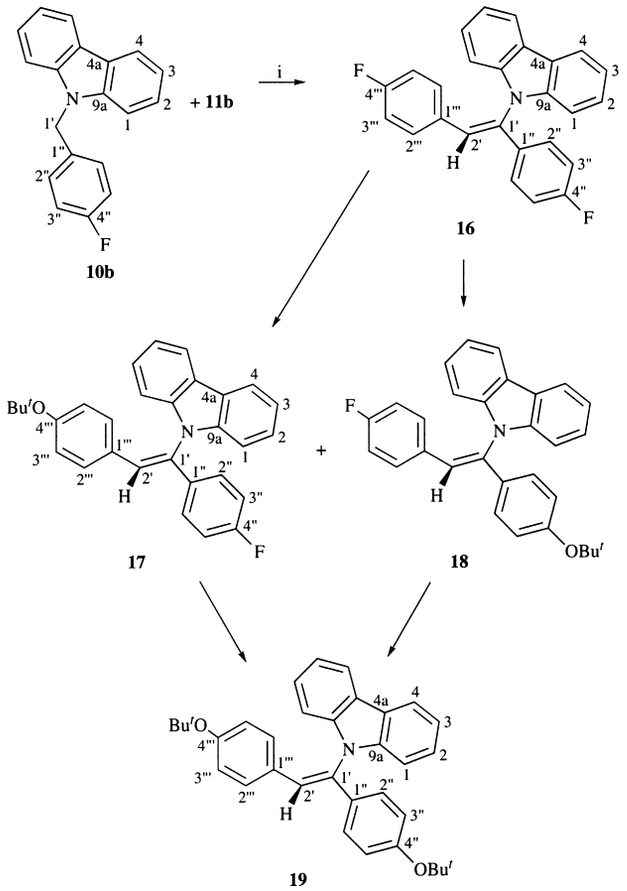
–PhNH$_2$, 100% conversion, i

15 (1′*E*,3′*E*)-dienamine **14** (1′*Z*,3′*E*)-dienamine

a Ar = **b** Ar = **c** Ar =

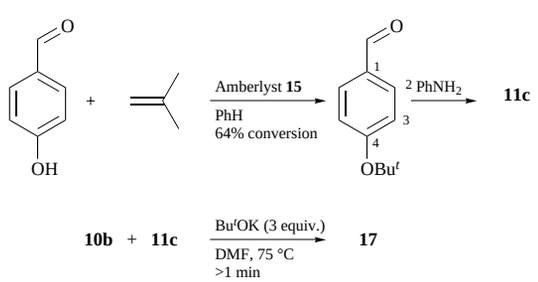
Scheme 3 *Reagents and conditions:* i, DMF (50 cm^3), Bu^{t}OK (1 equiv.), 0–75 °C, <3 min

condensation step leading to **16**. We have employed this facile displacement to prepare polymers from **16** by reaction with bisphenols, to be reported elsewhere. Earlier we reported a similar sequence to that shown in Scheme 4, for the preparation of bis(4-fluorophenyl)acetylene and the displacement of fluorines.[3] By way of comparison, **16** is at least three times less reactive in the fluorine displacement reaction than bis(4-fluorophenyl)acetylene. Only the *Z*-isomers (*vide infra*) of **16**–**19** are shown in Scheme 4 since these are by far the predominant isomers (*Z*-isomer >95% estimated by HPLC area of peaks) and the only ones isolated. By working up the reaction quickly by pouring the mixture into water, the amount of **16** is maximized and may be separated by column chromatography from minor concentrations of species **17–19**. Enamine **19** can also be easily separated by letting the reaction run to



Scheme 4 *Reagents and conditions:* i, DMF, Bu^{t}OK (3 equiv.), 75 °C, <1 min

completion over a 12 h period at 75 °C and/or by having a larger excess of Bu^{t}OK present to expedite the completion of the reaction. However, **17** and **18** cannot be easily separated from the complex mixture of products from the reaction of **10b** and **11b** because **17** and **18** have very similar properties in the chromatographic separation. Thus, we prepared **17** by the reaction of **10b** and **11c** by the reaction sequence shown in Scheme 5.



Scheme 5

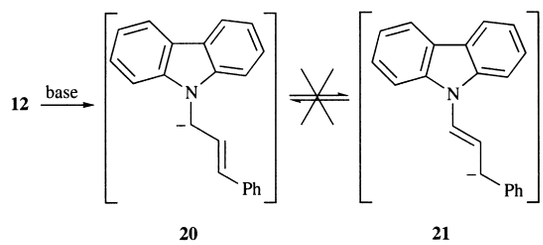
Structural evidence for 14 and 15

During the course of the synthesis of **14** and **15** we noted a large disparity in their retention times (t_R) of up to 3 min. In contrast, for enamines **16**–**19**, Δt_R is *ca.* 0.3 min. Only the more polar *Z*-isomer, 95% of the product by HPLC, was isolated and characterized.

Alkylation of carbazole with *trans*-cinnamoyl chloride leads to the *trans* product **12** ($J_{2',3'}$ = 16.1 Hz).[19a] Compound **12**, in turn, condenses with **13a** to produce **14** and **15**. The isomeric ratios for this reaction were 73:27, 85:15 and 90:10 for **14a**:**15a**, **14b**:**15b** and **14c**:**15c**, respectively, at 75 °C (HPLC) and do not vary when the reaction temperature is changed from 0 to 50 °C.

The mass spectra of **14a** and **15a** both show molecular ions at *m*/*z* 421, and very similar fragmentation patterns. UV spectroscopic data all show minor differences attributable to the different degree of twisting of the butadiene moiety. Noteworthy are the infrared bands, probably =CH vibrations[19b,c] or C–N stretches,[19d] at 1390 cm^{-1} in the spectra of the 1′*Z*-isomers and 1375 cm^{-1} in the spectra of the 1′*E*-isomers.

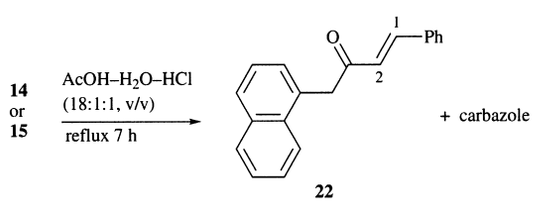
The fact that only two products **14** and **15** arise from the reaction suggests that there is no isomerization of the intermediate anion **20** to **21** (Scheme 6), which would result in the



Scheme 6

formation of additional isomeric products, although the isomerization of phenylmethylamino or dimethylamino analogues of **12** to their respective enamines in a strongly basic medium is the preferred process.[20]

Slow hydrolysis of **14** and **15** gives the identical α,β-unsaturated ketone **22** (NMR, MS, HRMS) (Scheme 7). The



Scheme 7

ketone **22** could not be completely isolated from the contaminating co-product carbazole, even after two attempts at column separations. The ^{1}H NMR spectrum of the mixture of **22** and carbazole also corroborates that the conformation about the carbon–carbon double bond in **22** is *trans* (J = 16 Hz) and is thus unaffected by the sequence of steps: tertiary amine ⟶ enamine ⟶ hydrolysis product.

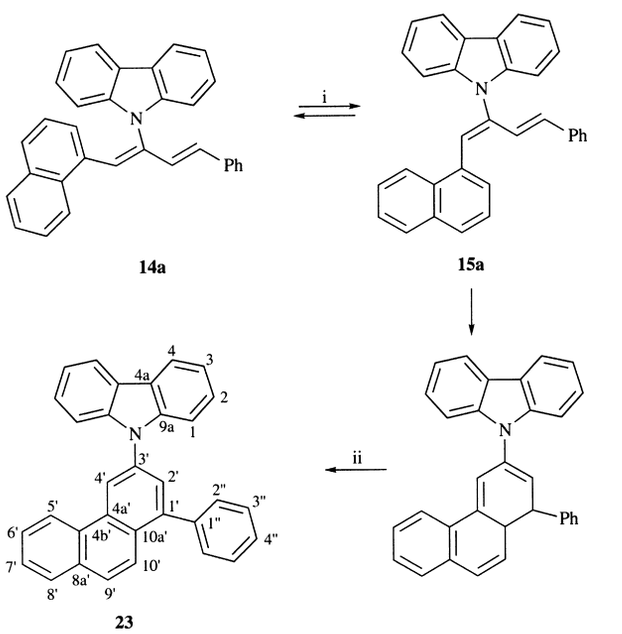
Attempted Diels–Alder reactions of **14a** and **15a** with maleic anhydride failed. Neither isomer reacted, even after 24 h in *o*-xylene when heated under reflux. In this reaction some of the more polar species were converted to the less polar compound, presumably by acid catalysed rearrangement, thermal rearrangement or both. This equilibration was also observed in the NMR experiments in $CDCl_3$ at room temperature.

Thermal behaviour

Following these observations, we decided to study the thermal behaviour of **14a**,**c** and **15a**,**c** by HPLC. *N*,*N*-Dimethylacetamide (DMAc) as solvent was our first choice because it has a relatively high boiling point and is the one which we have used successfully in polymerizations and making derivatives of difluoro enamines such as **16**. For these synthetic scale reactions no hydrolysis was detected, whereas at 160 °C the enamines **14** and **15** completely decomposed to give carbazole and other unidentified products, presumably by hydrolysis due to the small amount of water contained in DMAc.

However, in the absence of water the behaviour of **14a** and **15a** is quite different. In 1,2,4-trichlorobenzene, **14a** and **15a** partly equilibrate. In two independent experiments, on a micromolar scale, one beginning with **14a** and the other with **15a** in 1,2,4-trichlorobenzene at 180 °C, each first equilibrates with its isomer. With time another species appears (t_R = 10.2

min) and eventually becomes the predominant species in the mixture over a period of nine days. This experiment was repeated on a 0.5 g scale in order to identify the product. Thus, **14a** was heated in 1,2,4-trichlorobenzene under reflux for 4 days. The HPLC chromatograms at various times indicated an 88% conversion after 4 days. The workup of the mixture led to the isolation of the carbazolyl-substituted phenylphenanthrene **23** whose structure has been assigned pending complete characterization. It presumably arises from an intramolecular Diels–Alder reaction and subsequent air oxidation. The proposed sequence of steps is illustrated in Scheme 8.



Scheme 8 *Reagents and conditions:* i, 1,2,4-trichlorobenzene, 180 °C, 103 h; ii, air

In 1,2,4-trichlorobenzene at 180 °C, **14c** and **15c** behave as equilibrium species, over 4 days, with a minor amount of decomposition (3–5%) judging from a peak at $t_R = 2.27$ min which may be attributed to carbazole. Again carrying out two independent experiments on a micromolar scale, in which **14c** is added to one test tube and **15c** to another at 180 ± 1 °C, the approach to equilibrium may be followed by taking aliquots at different times and analysing them by HPLC (see Experimental for details). From the assumed first order isomerization, the integrated rate expressions[21] give estimates of the forward (k_f) and reverse (k_r) rate constants, with $(k_r + k_f) = 5.8 \times 10^{-6}$ s^{-1} and an equilibrium mole fraction of **14c** of 0.56. From these values the equilibrium constant K (= **14c**/**14c**) equals 0.77 and the rate constants k_f and k_r are 2.5×10^{-6} and 3.3×10^{-6} s^{-1}, respectively. Thus, **14c** and **15c** are interconvertable isomers with the 1′*Z*-isomer **14c** being the thermodynamically preferred isomer.

NMR Spectral analyses of *E*/*Z*-isomers

For enamines **14**–**17** and **21**, ^{1}H, ^{13}C, H-COSY, HMQC and HMBC experiments were necessary to identify the resonances of carbons and hydrogens in the ethane and butadiene moieties. Thus we were able to identify the arrangement of H1′ and C3′ in **14** and **15**, through the $^3J_{C3',H1'}$ coupling constants[22,23] listed in Table 1.

For the coupled ^{13}C NMR spectrum of **14a**, overlap of resonance lines renders the determination of the coupling constant doubtful, with $^3J_{C3',H1'} = 6.6$ Hz being towards the high end of a *cis* arrangement of C3′ and H1′. However, for this molecule we were able to confirm structure **14a** by X-ray crystallography. Its isomer **15a** shows $^3J_{C3',H1'} = 7.7$ Hz, a value definitely within the region of a *trans* arrangement of C3′ and H1′. The geometry is thus *E* at position 1′.

Table 1 Coupling constants ($^nJ_{C,H}$) for **14** and **15** in $CDCl_3$ from coupled/decoupled ^{13}C NMR[a] spectra

	$^1J_{C3',H3'}$/Hz	$^2J_{C3',H4'}$/Hz	$^3J_{C3',H1'}$/Hz
14a	153.1	2	6.6
14b	152.0	—	4.4
14c[b]	155.2	1.8	6.0
15a	154.2	2.2	7.7
15c[b]	153.8	—	8.2

[a] 67.9 MHz. [b] 125.7 MHz.

Compound **14b** shows $^3J_{C3',H1'} = 4.4$ Hz, a value representative of a *cis* arrangement of the carbon and hydrogen atoms at positions 3′ and 1′, respectively.

For **14c**, $^3J_{C3',H1'} = 5.9$ Hz, a coupling constant which is towards the high end of a *cis* arrangement of the C3′ and H1′ atoms. Thus the geometry for **14c** is likely to be 1′*Z*. Its corresponding isomer **15c** shows $^3J_{C3',H1'} = 8.2$ Hz, which is unmistakably a coupling constant resulting from a 1′*E* arrangement. For this molecule we were able to grow a single crystal from which an X-ray crystal structure was obtained (see below), which confirms the postulated 1′*E* geometry.

For species **19**, a difference NOE experiment was consistent with the structure of the *Z*-isomer. Thus the fluorine displacement reaction by *tert*-butoxide takes place without a detectable change in isomerism since the starting difluoro enamine **16** has the 1′*Z* geometry as shown by the X-ray structure (see below).

The large shielding effects[24,25] (1.23 and 0.84 ppm) experienced by H2″ and H3″, respectively, for **14a** relative to the cognates in **15a**, strongly suggest that these hydrogens in **14a** must be sited over the carbazole ring with little rotation possible for the naphthalene moiety. For the pair **14c** and **15c**, a somewhat smaller shielding of H2″ and H3″ (0.85 and 0.54 ppm, respectively) for **14c** relative to the cognates in **15c** similarly suggests that **14c** has the 1′*Z* arrangement. The latter shielding values are smaller, consistent with an averaging effect possible with increased rotation of the C1′-phenyl ring in **14c**.

Crystal structures

The single crystal of **14a** from which the X-ray structure was resolved was obtained by recrystallization from ethyl acetate and is represented in the CAChe™† model in Fig. 1. The ^{1}H NMR spectrum of this recrystallized sample suggests that the ratio of the dienamine molecules to ethyl acetate is 2:1, as does the unit cell. The plane of the heterocycle forms an acute dihedral angle with the plane defined by N–C2′–C1′ of 64°. The diene moiety deviates from coplanarity by *ca.* 15°. The plane of the naphthyl ring system is twisted from the C1″–C1′–C2′ plane by *ca.* 39°. The plane of the phenyl group is twisted from the C1‴–C4′–C3′ by *ca.* 6°. However, the larger deviations from coplanarity of the conjugated system for **14a** gives support to the UV interpretation for the reduced absorptivity for **14a** compared to **14b** and **14c**.

Two conformations A and B are adopted by the molecule **15c**, displayed in the CAChe† model in Fig. 2. The plane of the heterocycle is twisted by *ca.* 60° from the plane containing C1′–C2′–N for conformations A and B. The diene moiety is not coplanar by *ca.* 23° for A and *ca.* 25° for B. The phenyl ring at C1′ is twisted out of the plane defined by C1″–C1′–C2′ by 13° for A and 28° for B. The other phenyl ring at C4′ is twisted from the plane defined by C1″–C4′–C3′ by 22° for A and 16° for B.

We observe that the crystal of **15c** reflects a fluorescent blue colour when 365 nm wavelength light is shone on it, whereas the 1′*Z*-isomer is transparent. This phenomenon may be used to manually separate crystals of the 1′*E*-isomer in a mixture of 1′*E*- and 1′*Z*-isomers once this mixture, 85% enriched with the 1′*E*-isomer, is carefully crystallized.

† CAChe, ver. 3.6, from CAChe Scientific, Inc, 1994.

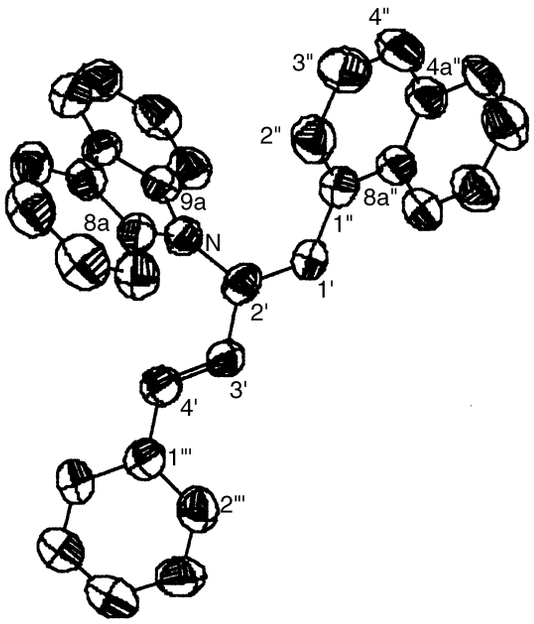


Fig. 1 ORTEP-type drawing from CAChe of **14a** without ethyl acetate solvent showing. The thermal ellipsoids are drawn with a probability value of 0.50. The atom labels shown are consistent with numbering in text.

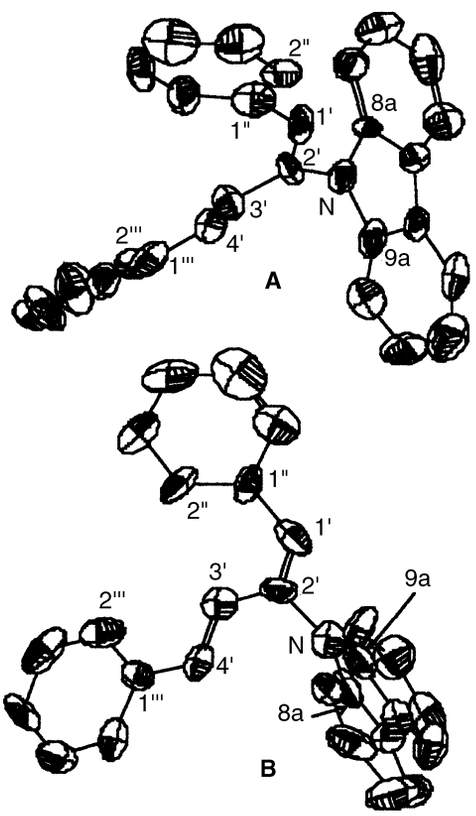


Fig. 2 ORTEP-type drawing from CAChe of dienamine **15c** crystallizing into two conformations **A** and **B** (50 : 50). The thermal ellipsoids are drawn with a probability value of 0.50. These are the relative positions of the conformers in the unit cell. The atom labels shown are consistent with numbering in text.

The crystal structure of compound **16** confirms its structure as that of the 1′*Z*-isomer, as shown in the CAChe† model in Fig. 3. The carbazolyl moiety is staggered by about 63° from the plane containing the double bond and the nitrogen atom. This also appears to be the preferred conformation in solution by analogy to the dienamines. Thus, little conjugation exists with the substituted stilbenyl moiety and the carbazolyl system. The

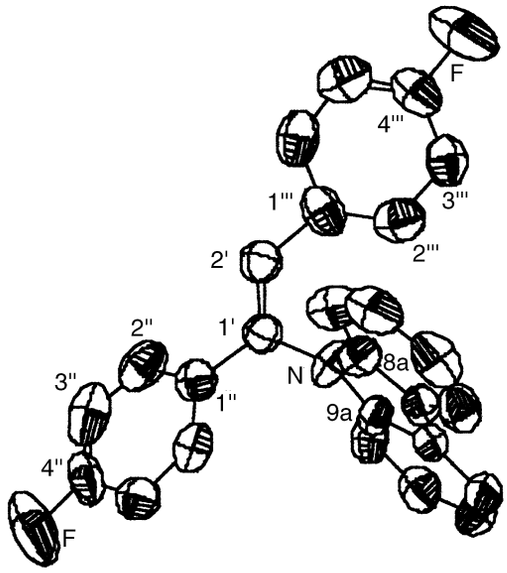


Fig. 3 ORTEP-type drawing from CAChe of the predominant (71%) conformer of **16**. The thermal ellipsoids are drawn with a probability value of 0.50. The atom labels shown are consistent with numbering in text.

plane of the fluorophenyl ring bonded to C1′ is not coplanar with the double bond C1′–C2′ and atom C1″ with a dihedral angle of 26°. The fluorophenyl moiety at C2′ is also twisted from the plane C1″–C2′–C1′ by 23°. The fluorophenyl groups are out of plane, *i.e.* C1″ is out of the plane defined by C1′–C2′–C1‴ by 8°.

Conclusions

NMR Techniques and crystal data for some of the enamines and dienamines convincingly define their geometry. A novel reaction leads to the predominant formation of the 1′*Z*-isomer regardless of greater steric constraints imposed by bulkier aryl and carbazolyl groups. This is probably a result of the greater conjugation energy gained by the enamines through the aromatic groups with little, if any, cross-conjugation with the heterocycle. Hydrolysis, equilibration and rearrangements occur very slowly under unusually stringent conditions. In retrospect the predominant 1′*Z*-isomers, which also probably form in the syntheses of the analogous benzotriazoles and benzimidazole enamines,[4] are endowed with the right geometry for the *anti* elimination of the nitrogen heterocycle making possible the formation of diarylacetylenes in the presence of strong base.[3,4]

Experimental

X-Ray structure determination‡

The crystals used for the X-ray study were grown by routine recrystallization from acetonitrile, ethyl acetate and MeOH for **16**, **14a** and **15c** respectively. The crystal data, parameters of data collection and refinement results are given in Table 2. The unit cell dimensions were determined by least-squares using 25 (for **16** and **14a**) and 15 (for **15c**) centred reflections using graphite monochromated Cu-Kα radiation. Data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.53319E-5 for **16**, 0.888854E-5 for **14a**, 0.148 for **15c**). No correction was made for absorption for **15c**. The structures for **16**, **14a** and **15c** were solved by direct methods. The non-hydrogen atoms (for **16** and **14a**) were refined anisotropically.

‡ Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/92.

Table 2 Crystal data, data collection and refinement parameters

	14a·1/2(CH_3CO_2Et)	**15c**	**18**
Formula	$C_{34}H_{27}NO$	$C_{28}H_{21}N$	$C_{26}H_{17}F_2N$
Mass	465.59	371.48	381.42
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*2/*c* (no. 13)	*Pna*21 (no. 33)	$P2_1/c$ (no. 14)
Dimensions/mm	0.50 × 0.22 × 0.12	0.25 × 0.15 × 0.05	0.37 × 0.125 × 0.45
a/Å	16.120(2)	10.239(4)	15.808(3)
b/Å	8.928(2)	23.066(3)	10.728(2)
c/Å	18.517(2)	17.529(3)	11.650(2)
β (°)	106.471(9)	90	104.70(1)
Z	4	8 (*z*′ = 8)	4
V/Å^3	2556(1)	4139.9(19)	1911(1)
ρ (calc.)/g cm^{-3}	1.21	1.192	1.326
Radiation	Cu-Kα	Cu-Kα	Cu-Kα
μ/cm^{-1}	5.22	4.9	7.1
Method/Trans max	psi 0.96 to 1.00	None	psi 0.91 to 1.00
F(000)/e	984	1568	792
T/K	294	294	294
Diffractometer	AFC6S (Rigaku)	AFC6S (Rigaku)	AFC6S (Rigaku)
Index ranges	*h*, *k*, ± *l*	*h*, *k*, *l*/ −*h*, −*k*, −*l*	*h*, *k*, ±*l*
Scan mode, speed/degrees min^{-1}	ω–2θ, 16	ω/2θ, 4	ω–2θ, 16
2θ range (°)	45–55	40–50	55–60
Total data collected	5154	4630	3093
Unique data	4977	2320	2929
Observed data used	1693 [$I > 3\sigma$(I)]	1803 [$I > 2\sigma(I)$]	1429 [$I > 3\sigma(I)$]
System used	TEXSAN[a]	NRCVAX[b]	TEXSAN[a]
No. of parameters refined	348	263	329
Final shift/error (maximum and average)	0.18, 0.00	0.251, NA	1.8, 0.08
Max residual density/e Å^{-3}	−0.17 to +0.24	−0.17 to +0.18	−0.19 to +0.25
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.06	0.052	0.048
$R_w = [\Sigma\omega(\|F_o\| - \|F_c\|)^2/\Sigma\omega(\|F_o\|^2)]^{0.5}$	0.07	0.031	0.042
GOF = $[\Sigma\omega(\|F_o\| - \|F_c\|)^2/(N_o - N_v)]^{0.5}$	1.89	1.34	1.7

[a] TEXRAY Structure Analysis Package, Molecular Structure Corporation 1985. [b] Full System Reference, see ref. 26.

The molecule **16** is disordered over two orientations with populations of 71 and 29%.§ The disordered atoms are C1′ and C2′ (labels in **16**). No disorder was resolved for the phenyl rings attached to these carbons. Disordered atoms were refined isotropically and H2′ was introduced at a calculated position and was not refined. All other hydrogens were located on difference Fourier maps and were refined isotropically.

The molecule **14a** crystallizes with the solvent ethyl acetate in the proportion 2:1. The ethyl acetate molecule is disordered over two orientations about the two-fold axis. Each orientation corresponds to 50% occupancy. No atoms are on the axis but the methylene and carbonyl carbons are close. The carbonyl carbon was refined isotropically because of its proximity to the two-fold axis. Hydrogen atoms in the solvent molecule were not included in the model.

Refinement for **15c** was carried out in blocks of one molecule at a time, all non-hydrogen atoms were refined anisotropically, hydrogen atoms were introduced at idealized geometries [C–H = 0.95 Å and U_{iso}(H) = 1.1 U(eq)C + 0.01]. Acentricity in this crystal comes from packing, not from the molecule.

Instruments and techniques

^{1}H, ^{13}C, H–C HETCOR and H-decoupling NMR experiments were recorded at room temperature on Varian 500 Unity NMR or JEOL-270 spectrometers. Usually 30–50 mg of sample was dissolved in 1.0 cm^3 of $CDCl_3$ and the solvent resonance was used as the internal lock. For the ^{1}H NMR determinations tetramethylsilane was used as the internal standard. Carbon and hydrogen NMR assignments on the Varian 500 Unity were determined with the aid of H-COSY, HMQC and HMBC techniques as described recently for other materials.[27] The numbers refer to the position of the carbon or hydrogen as illustrated in the respective structures (see text). HETCOR and COLOC experiments were used on the JEOL-270 spectrometer for the partial assignments of **14b**. The data are listed in Table 3. The IR spectra (32 scans) were recorded on an Analect Instruments AQS-18 FTIR spectrometer at a resolution of 2 cm^{-1} in $CDCl_3$ solution at *ca.* 0.01 M concentration at room temperature in a KBr cell of *ca.* 0.05 mm path length. The UV measurements were made on a Unicam SP800 spectrophotometer in MeOH solution at 25 °C (Table 4). A Milton Roy® CM4000 multiple solvent delivery system equipped with spectroMonitor® 3100 variable wavelength detector and CI-10B integrator was used to run HPLC chromatograms using reverse-phase columns at a MeOH flow rate of 1 cm^3 min^{-1}.

Materials

Carbazole (Pfaltz & Bauer), cinnamoyl chloride, 4-fluorobenzyl chloride (Lancaster), Bu^{t}OK (Aldrich), DMF (BDH) and 2-methylpropene (Matheson) were used without further purification. All chromatographic separations were performed using silica gel 260 (BDH) unless otherwise specified. Compounds **10a**,[4] **11b**[2] and **13**[17] were prepared as outlined earlier. Elemental analyses are listed in Table 5.

9-(4-Fluorobenzyl)-9*H*-carbazole 10b

Anhydrous K_2CO_3 (22.1 g, 0.160 mol) and KOH (33.8 g, 0.500 mol) were blended, powdered and added to tetrabutylammonium hydrogen sulfate (3.39 g, 0.01 mol). To this mixture was added carbazole (16.7 g, 0.100 mol), toluene (300 cm^3) and 4-fluorobenzyl chloride (14.5 g, 0.100 mol). This mixture was stirred at 80 °C for 1 h, filtered hot and the solids washed with toluene (100 cm^3). The filtrate was evaporated and the solid residue (24.1 g, 87.5%) recrystallized from MeOH (*ca.* 1 dm^3). The second recrystallization of a small sample gave plates, mp 124–125 °C (MeOH).

(4-*tert*-Butoxybenzylidine)aniline 11c

4-Hydroxybenzaldehyde, recrystallized from H_2O and then benzene (10 g, 0.082 mol), was dissolved in benzene (600 cm^3). To this solution, while stirring at 45 °C but without any other external heat, was added Amberlyst 15 (BDH, 2.5 g) and

§ The minor orientation has a large error value associated with it.

Table 3 NMR spectroscopic data for novel products[a]

Product	δ_C(*J*/Hz, assignment[b])	δ_H(multiplicity, *J*/Hz, assignment[b])
10b	45.00 (1′), 109.66 (1), 115.52 ($J_{C3',F}$ 21.1, 3″), 119.27 (3), 120.53 (4), 122.45 (4a), 126.05 (2), 128.92 ($J_{C2'',F}$ 8.2, 2″), 134.17 ($J_{C1'',F}$ 3.7, 1″), 140.21 (9a), 161.53 ($J_{C4'',F}$ 242.7, 4″).	5.62 (s, 2 H, 1′), 7.06 (t, *J* 8.8, 2 H), 7.20 (t, 4 H), 7.42 (t, 2 H), 7.62 (d, 2 H, 1), 8.16 (d, *J* 7.8, 2 H, 4).
4-Bu^{t}OC$_6$H$_4$CHO	28.81 (CH_3), 79.85 (CMe_3), 122.26 (3), 130.94 (1), 131.11 (2), 161.62 (4), 190.93 (CHO).	1.44 (s, 9 H, CH_3 × 3), 7.10 (d, $J_{2,3}$ 8.5, 2 H, 3), 7.80 (d, $J_{2,3}$ 8.5, 2 H, 2), 9.91 (s, 1 H, COH).
12	44.37 (1′), 109.61 (1), 119.11 (3), 120.48 (4), 122.45 (4a), 124.84 (2′), 125.93 (2), 126.39 (2″), 127.76 (4″), 128.68 (3″), 131.4 (3′), 136.16 (1″), 140.13 (9a).	5.15 (d, *J* 6.37, 2 H, 1′), 5.61 (d, $J_{2',3'}$ 16.11, 1 H, 3′), 6.38 (tt, *J* 5.86, $J_{2',3'}$ 16.11, 1 H, 2′), 7.14–7.27 (m, 7 H, 3 and 2″–4″), 7.46 (t, $J_{1,2} = J_{2,3}$ = 7.5, 2 H, 2), 7.63 (d, $J_{1,2}$ 7.81, 2 H, 1), 8.18 (d, $J_{3,4}$ 7.81, 2 H, 4).
14a	110.62 (1), 119.6 (3), 120.12 (4), 123.3 (4a), 123.41 (8″), 125.17 (2″), 125.35 (3″), 125.65 (6″), 125.88 (2), 126.33 (7″), 126.52 (3′), 126.81 (2″), 128.04 (4‴), 128.25(1′), 128.44 (4″), 128.58 (3‴), 128.77 (5″), 130.82 (1″), 131.25 (4′), 131.35 (8a″), 133.35 (4a″), 135.28 (2′), 136.28 (1‴), 139.91 (9a).	6.05 (d, $J_{3',4'}$16.1, 1 H, 4′), 6.60 (d, $J_{2'',3''}$ 7.3, 1 H, 2″), 6.75 (t, $J_{2'',3''} = J_{3'',4''}$ = 7.8, 1 H, 3″), 7.16–7.28 (m, 11 H, 1–3 and 2‴–4‴), 7.31 (d, $J_{3',4'}$ 15.7, 1 H, 3′), 7.45 (br d, 2 H, 4″ and 6″), 7.56 (t, $J_{6'',7''}$ 7.5, 1 H, 7″), 7.70 (d, $J_{5'',6''}$ 7.8, 1 H, 5″), 7.75 (s, 1 H, 1′), 8.07 (d, $J_{3,4}$ 7.3, 2 H, 4), 8.27 (d, $J_{7'',8''}$ 8.3, 1 H, 8″).
14b	55.02 (CH_3), 110.51 (1), 113.94 (3″), 119.69 (3), 120.25 (4), 123.29 (9a), 126.05 (2), 126.58 (2‴ or 3‴), 126.85 (1″), 127.09 (3′), 128.48 (2‴ or 3‴), 129.29 (4′), 130.23 (2″), 131.34 (2′), 131.59 (1′), 136.51 (1‴), 139.27 (4a), 159.38 (4″).	3.62 (s, 3 H, CH_3), 5.72 (d, $J_{3',4'}$ 15.8, 1 H, 4′), 6.44 (d, $J_{2'',3''}$ 8.6, 2 H, 3″), 6.58 (d, $J_{2'',3''}$ 9.0, 2 H, 2″), 7.01 (s, 1 H, 1′), 7.10–7.30 (m, 11 H), 7.13 (d, 1 H, 3′), 8.14 (d, $J_{3,4}$ 7.9, 2 H, 4).
14c[c]	110.52 (1), 119.78 (3), 120.26 (4), 123.36 (4a), 126.72 (2), 126.72 (2‴), 126.8 (3′), 127.9 (4‴), 128.14 (4″), 128.42 (3″), 128.5 (3‴), 128.62 (2″), 130.57 (4′), 131.84 (1′), 133.48 (2′), 134.11 (1″), 136.28 (1‴), 139.31 (9a).	5.85 (d, $J_{3',4'}$ 16.11, 1 H, 4′), 6.68 (d, $J_{2'',3''}$ 7.3, 2 H, 2″), 6.92 (t, $J_{2'',3''} = J_{3'',4''}$ = 7.3, 2 H, 3″), 6.97 (d, 1 H, 4″), 7.07 (s, 1 H, 1′), 7.16 (d, $J_{3',4'}$ 16.11, 1 H, 3′), 7.16–7.26 (m, 9 H, 1 and 3 and 2‴–4‴), 7.31 (t, $J_{2,3} = J_{1,2}$ = 7.8, 2 H, 2), 8.16 (d, $J_{3,4}$ 7.8, 2 H, 4).
15a	110.45 (1), 119.72 (3), 120.3 (4), 121.6 (3′), 123.26 (4a), 124.71 (8″), 125.41 (3″), 126.02 (2), 126.3 (6″), 126.59 (7″), 126.94 (2‴), 128.13 (4‴), 128.28 (2″), 128.5 (3‴), 128.61 (4″), 128.84 (5″), 130.33 (1′), 131.88 (8a″), 132.52 (1″), 133 (4′), 133.68 (4a″), 136.28 (1‴), 136.61 (2′), 141.3 (9a).	6.21 (d, $J_{3',4'}$ 16.1, 1 H, 4′), 7.09 (m, 5 H, 2‴–4‴), 7.30 (t, $J_{2,3} = J_{3,4}$ = 7.3, 2 H, 3), 7.37 (d,[d] 1 H, 3′), 7.39 (s,[d] 1 H, 1′), 7.44 (t, $J_{1,2} = J_{2,3}$ = 7.3, 2 H, 2), 7.47–7.54 (m, 4 H, 1 and 6″–7″), 7.59 (t, $J_{2'',3''} = J_{3'',4''}$ = 7.5, 1 H, 3″), 7.83 (d, $J_{2'',3''}$ 7, 1 H, 2″), 7.90 (d, $J_{3'',4''}$ 7,[e] 2 H, 4″–5″), 7.99 (d, $J_{7'',8''}$ 8.8, 1 H, 8″), 8.18 (d, $J_{3,3}$ 7.3, 2 H, 4).
15c	110.51 (1), 119.65 (3), 120.21 (4), 121.28 (3′), 123.21 (4a), 125.89 (2), 126.97 (2‴), 128.04 (4″), 128.2 (4″), 128.58 (3‴), 128.71 (3″), 129.56 (2‴), 131.96 (1′), 133.33 (4′), 135.04 (2′), 135.69 (1″), 136.36 (1‴), 141.18 (9a).	6.19 (d, $J_{3',4'}$ 16.1, 1 H, 4′), 6.85 (s, 1 H, 1′), 7.15–7.20 (m, 5 H, 2‴–4‴), 7.26 (dd, $J_{2,3} = J_{3,4}$ = 7.8, 2 H, 3), 7.28–7.35 (t, 1 H, 4″), 7.38 (t, $J_{1,2} = J_{2,3}$ = 7.5, 2 H, 2), 7.42 (d, $J_{1,2}$ 7.5, 2 H, 1), 7.46 (t, $J_{2'',3''} = J_{3'',4''}$ = 7.5, 2 H, 3″), 7.52 (d, $J_{3',4'}$ 16.1, 1 H, 3′), 7.53–7.56 (br d, 2 H, 2″), 8.14 (d, $J_{3,4}$ 8.3, 2 H, 4).
16	110.91 (1), 115.44 ($J_{C3''',F4'''}$ 21.1, 3‴), 115.8 ($J_{C3'',F4''}$ 22, 3″), 120.19 (3), 120.31 (4), 123.72 (4a), 125.78 (2′), 126.07 (2), 127.71 ($J_{C2'',F4''}$ 8.2, 2″), 130.17 ($J_{C2''',F4'''}$ 8.2, 2‴), 130.8 ($J_{C3''',F4'''}$ 2.7, 1‴), 132.57 ($J_{C1',F4''}$ 1.8, 1′), 133.7 ($J_{C1',F4''}$ 3.7, 1″), 139.2 (9a), 162.03 ($J_{C4''',F4'''}$ 249.1, 4‴), 163.03 ($J_{C4'',F4''}$ 249.1, 4″).	6.66 (t, $J_{2'',3'''} = J_{H3''',F'''}$ = 8.8, 2 H, 3‴), 6.80 (dd, $J_{2''',3'''}$ 8.8, $J_{H2''',F4''}$ 5.4, 2 H, 2‴), 6.93 (t, $J_{2'',3''} = J_{H3'',F4''}$ = 8.8, 2 H, 3″), 7.02 (d, $J_{1,2}$ 7.8, 2 H, 1), 7.16 (dd, $J_{2'',3''}$ 9, $J_{H2'',F4''}$ 5, 2 H, 2″), 7.21 (s, 1 H, 2′), 7.22–7.27 (m, 4 H, 2 and 3), 8.12 (d, $J_{3,4}$ 8.3, 2 H, 4).
17	28.71 (CH_3), 78.72 (CMe_3), 111.09 (1), 115.72 ($J_{C3'',F}$ 21.1, 3″), 119.98 (3), 120.18 (4), 123.68 (3‴), 125.9 (2), 126.54[f] (4a), 126.56[f] (2′), 127.57 ($J_{C2'',F}$ 8.2, 2″), 129.19 (3‴), 129.69 (1‴), 131.57 (1′), 134.05 ($J_{C1',F}$ 3.7, 1″), 139.33 (9a), 155.31 (4‴), 162.85 ($J_{C4'',F}$ 249.1, 4″).	1.18 (s, 9 H, CH_3 × 3), 6.59 (d, $J_{2''',3'''}$ 8.3, 2 H, 3‴), 6.72 (d, $J_{2''',3'''}$ 8.5, 2 H, 2‴), 6.93 (dd, $J_{2'',3''}$ 8.8, $J_{3'',F}$ 8.5, 2 H, 3″), 7.02 (d, $J_{1,2}$ 8.3, 2 H, 1), 7.17 (dd, $J_{2'',3''}$ 8.5, $J_{2'',F}$ 5.4, 2 H, 2″), 7.20–7.25 (m, 5 H, 2, 3 and 2′),[g] 8.12 (d, $J_{3,4}$ 8.8, 2 H, 4).
19	28.72 and 28.84 (CH_3), 78.62 and 78.77 (CMe_3), 111.24 (1), 119.77 (3), 120.05 (4), 123.58 (4a), 123.68 (3‴), 123.82 (3″), 125.52 (2′), 125.78 (2), 126.51 (2″), 129.04 (2‴), 130.06 (1‴), 132.34 (1′), 132.63 (1″), 139.5 (9a), 155.02 (4‴), 156.04 (4″).	1.22 (s, 9 H, CH_3 × 3), 1.35 (s, 9 H, CH_3 × 3), 6.62 (d, $J_{2''',3'''}$ 8.5, 2 H, 3‴), 6.73 (d, $J_{2''',3''}$ 8.8, 2 H, 2‴), 6.90 (d, $J_{2'',3''}$ 8.8, 2 H, 3″), 7.08 (d, $J_{1,2}$ 7.8, 2 H, 1), 7.15 (d, $J_{2'',3''}$ 8.8, 2 H, 2″), 7.22–7.28 (m, 5 H, 2, 3 and 2′), 8.12 (d, $J_{3,4}$ 8, 2 H, 4).
23	109.82 (1), 120.12 (3), 120.23 (4′), 120.42 (4), 123.06 (5′), 123.53 (4a), 124.31, 126.10 (2), 126.60 (2′) 126.99, 127.30, 127.42 (8′), 127.70 (4″), 128.46 (3″), 128.62, 129.02, (8a′ or 10a′), 130.07, (4b′), 130.15 (2″), 132.00 (8a′ or 10a′), 132.04 (4a′), 135.36 (3′), 140.09 (1″), 141.12 (9a), 143.00 (1′).	7.32 (t, *J* 7.8, 2 H, 3), 7.44 (t, *J* 8.3, 2 H, 2), 7.47 (t, *J* 7, 1 H, 4″), 7.53–7.62 (m, 6 H), 7.63–7.68 (m, 2 H), 7.75–7.78 (m, 2 H), 7.91–7.95 (m, 2 H), 8.20 (d, *J* 7.8, 2 H, 1), 8.64–8.67 (m, 1 H, 5′), 8.93 (d, *J* 1.5, 1 H, 4′).

[a] The ^{1}H NMR spectra at room temperature were referenced using $SiMe_4$ as the internal standard. The ^{13}C NMR spectra were referenced to the middle line of $CDCl_3$ at δ 77.00 as per ref. 23(*c*). Assignments were aided by H-COSY, HMQC (null = 0.65 s) and HMBC (taumb = 0.05 s) experiments similar to those recently described in ref. 27. [b] The atom numbering is indicated on the respective structures. [c] HMQC (null = 0.7 s). [d] Doublet and singlet are superimposed. [e] Two doublets with the same chemical shift. [f] Values may be interchanged. [g] From difference NOE experiment, H2′ resonates at δ 7.22.

2-methylpropene gas was bubbled slowly into the reaction for 17 h. An aliquot indicated a 64% conversion (HPLC). After this period the solution was filtered, the filtrate extracted with 10% NaOH (2 × 100 cm^3), washed with H_2O (2 × 100 cm^3) and dried over $MgSO_4$. The mixture was filtered and the filtrate evaporated. The residue weighed 11 g. This residue was adsorbed on alumina (basic) and chromatographed using light petroleum (bp 35–60 °C)–EtOAc (97 : 3) as eluent. Evaporation of the solvent from the later fractions gave 4-*tert*-butoxybenzaldehyde[28] (2.0 g) as an oil.

To 4-*tert*-butoxybenzaldehyde (2.0 g, 0.011 mol) was added aniline (1.04 g, 0.0110 mol) and benzene (30 cm^3), and the water was removed by azeotropic distillation in a Dean–Stark trap for 1 h. Unreacted aldehyde remained (HPLC) and aniline was added in increments of 0.2 cm^3 to the boiling benzene and distillation continued for 15 min after each addition. The ^{1}H NMR spectrum of the mixture, where the equilibrium is completely over to the imine side, shows *ca.* 75% mole excess of aniline. Attempted purification by chromatography using either silica gel or aluminum oxide (basic), with light petroleum–EtOAc (97 : 3) as eluent, gave a mixture containing 10–15% of the aldehyde by hydrolysis. Since an excess of aniline is not detrimental

Table 4 Spectroscopic data for novel products

Compound	*m/z* (%)	λ_{max}(MeOH)/nm (log *E*)
12		260 (4.41), 288 (4.02), 294 (4.16), 329 (3.49), 343 (3.55)
14a	421 (M^+, 100), 255 (26.6), 239 (16.9), 172 (22.8), 129 (45.9), 112 (15.8), 83 (40.3), 58 (38.9), 43 (56.4)	259 (4.31), 289 (4.35), 336 (4.45)
15a	421 (M^+, 100), 255 (28.1), 239 (17.6), 172 (24.3), 129 (17.6)	259 (4.34), 289 (4.49), 326 (4.33), 336 (4.32)
14b		260 (4.28), 293 (4.33), 337.5 (4.64)
14c		259 (sh, 4.23), 297.5 (4.42), 326 (4.62)
15c		255 (sh, 4.44), 291 (4.37), 318 (4.36)
23	HRMS: calc. for $C_{32}H_{21}N$ 419.167 39. Found, 419.167 20.	214 (4.99), 252 (4.95), 290 (4.55), 321 (4.35), 323 (4.33)

Table 5 Elemental microanalyses for the new compounds

Compound	Formula	Found (%)	Calculated (%)
10b	$C_{19}H_{14}FN$: *M*, 275.33	C, 82.42: H, 5.26; N, 4.84	C, 82.89; H, 5.13; N, 5.09
12	$C_{21}H_{17}N$: *M*, 283.38	C, 88.73; H, 6.17; N, 4.94	C, 89.01; H, 6.05; N, 4.94
14a	$C_{32}H_{23}N$: *M*, 421.55	C, 91.18; H, 5.60; N, 3.67	C, 91.18; H, 5.50; N, 3.32
15a	$C_{32}H_{23}N$: *M*, 421.55	C, 91.13; H, 5.71; N, 3.40	C, 91.18; H, 5.50; N, 3.32
14b	$C_{29}H_{23}NO$: *M*, 401.51	C, 86.71; H, 5.61; N, 3.45	C, 86.75; H, 5.77; N, 3.49
14c	$C_{28}H_{21}N$: *M*, 371.49	C, 90.26; H, 5.62; N, 3.68	C, 90.53; H, 5.70; N, 3.77
15c	$C_{28}H_{21}N$: *M*, 371.49	C, 89.98; H, 5.83; N, 3.74	C, 90.53; H, 5.70; N, 3.77
16	$C_{26}H_{17}F_2N$: *M*, 381.42	C, 81.77; H, 4.71; N, 3.65	C, 81.87; H, 4.49; N, 3.67
17	$C_{30}H_{26}FNO$: *M*, 435.54	C, 83.02; H, 6.04; N, 3.16	C, 83.73; H, 6.02; N, 3.22
19	$C_{34}H_{35}NO_2$: *M*, 489.66	C, 83.31; H, 7.37; N, 2.82	C, 83.40; H, 7.20; N, 2.86

for the enamine formation this mixture was used below, as prepared, with excess aniline.

(2′*E*)-9-(3′-Phenylprop-2′-enyl)-9*H*-carbazole 12

Following the procedure for the preparation of **10b**, but using cinnamoyl chloride (15.26 g, 0.10 mol) instead of 4-fluorobenzyl chloride, gave **12** (23.5 g, 83%), mp 147–150 °C (acetone).

(1′*Z*,3′*E*)- and (1′*E*, 3′*E*)-9-[1′-(1″-Naphthyl)-4′-phenylbuta-1′,3′-dien-2′-yl]-9*H*-carbazole 14a and 15a

A solution of **12** (2.83 g, 0.01 mol) and **13a** (2.60 g, 0.01 mol) in DMF (10 cm^3) was added to Bu^{t}OK (1.50 g, 0.0134 mol) in DMF (40 cm^3) at 75 °C. After 12 min the conversion was 100% by HPLC: the isomers had t_R = 5.44 (73%) and 9.07 min (27%). The solution was poured into H_2O (150 cm^3) and the solvent was decanted from the oily precipitate which was washed with H_2O. Chromatography using light petroleum–$CHCl_3$ (9:1) as eluent gave **15a** (t_R = 9.07 min) followed by **14a** (t_R = 5.44 min).

The eluted fractions which contained more than 90% of **15a** were combined, the solvent evaporated and the residue recrystallized twice from acetone to give **15a** as needles (23%), mp 189–190 °C.

Combination of the fractions containing **14a** and evaporation of the solvent left a residue. This was recrystallized from acetone to give clear prisms (2.65 g, 63%). When heated to 135 °C the compound effervesced and the prisms became opaque; upon further heating the prisms melted: mp 175–177 °C (acetone).

(1′*Z*,3′*E*)-9-[1′-(4″-Methoxyphenyl)-4′-phenylbuta-1′,3′-dien-2′-yl]-9*H*-carbazole 14b

Following the preparation for **14a** on a 0.01 mol scale, using **13b** instead of **13a**, gave after *ca.* 5 min a conversion of 100% by HPLC: the isomers had t_R = 4.69 (85%) and 6.46 min (15%). Similar workup as for **14a** and three recrystallizations from EtOAc gave **14b** (45%). An analytical sample was recrystallized from methanol, mp 185–187 °C.

(1′*Z*,3′*E*)- and (1′*E*,3′*E*)-9- [1′,4′-Diphenylbuta-1′,3′-dien-2′-yl]-9*H*-carbazole 14c and 15c

Following the preparation for **14a** on a 0.05 mol scale, using **13c** instead of **13a**, gave after *ca.* 2 min a conversion of 100% by HPLC: the isomers had t_R = 3.75 (90%) and 5.60 min (10%). Similar workup as for **14a** and chromatography of the precipitate on silica gel 60 using light petroleum–$CHCl_3$ (9:1) as eluent gave **15c** (t_R = 5.60 min) followed by **14c** (t_R = 3.75 min).

The eluted fractions which contained more than 93% of **15c** were combined, the solvent evaporated and the residue recrystallized three times from acetonitrile into clear prisms. The yield of this pure material was *ca.* 1%. The sample submitted for X-ray crystal structure analysis was recrystallized from MeOH. An analytical sample was recrystallized from acetone, mp 158–160 °C.

Eluted fractions which contained more than 85% of **14c** were combined, the solvent evaporated and the residue recrystallized three times from acetonitrile into clear prisms. The yield of this pure material was 45%. An analytical sample was recrystallized, mp 143–145 °C (MeOH).

(1′*Z*)-9-[1′,2′-Bis(4-fluorophenyl)ethenyl]-9*H*-carbazole 16

To a solution of Bu^{t}OK (6.72 g, 0.06 mol) in DMF (40 cm^3) at 75 °C was added a solution of **10b** (5.5 g, 0.02 mol) and **11b** (4.0 g, 0.02 mol) in DMF (10 cm^3), and the mixture was stirred at 75 °C for 1 min. After this period it was immediately poured into H_2O (200 cm^3). This mixture was stirred and the precipitate filtered off. The oily solid was dissolved in $CHCl_3$ (200 cm^3) and the solution dried over $MgSO_4$. The solution was filtered and the solvent evaporated. The residue was taken up in CCl_4 and chromatographed (CCl_4). The first fractions contained exclusively **16**. These were combined and the solvent evaporated. The residue (4.73 g, 62%) was recrystallized, mp 199 °C (acetonitrile).

(1′*Z*)-9-[2′-(4-*tert*-Butoxyphenyl)-1′-(4-fluorophenyl)ethenyl]-9*H*-carbazole 17

To a solution of Bu^{t}OK (3.3 g, 0.029 mol) in DMF (40 cm^3) at 75 °C was added a solution of **10b** (2.75 g, 0.01 mol) and **11c** (3 g of a mixture containing a *ca.* 75% mole excess of aniline, 0.0093 mol) in DMF (10 cm^3) and the mixture was stirred at 75 °C for 1 min. After this period it was immediately poured into water (150 cm^3). This mixture was extracted with diethyl ether (3 × 50 cm^3) and the solvent evaporated over 5 g of silica gel. The adsorbed material was chromatographed on 40 g of silica gel using light petroleum–EtOAc (97:3) as eluent. Unreacted **10b** eluted first followed by **17**. The fractions which contained greater than 85% of **17** (HPLC) were combined and the eluent evaporated.

Recrystallization from propan-2-ol gave 1.84 g (45%). An analytical sample was recrystallized three times from MeOH, mp 147–150 °C.

(1′*Z*)-9-[1′,2′-bis(4-*tert*-butoxyphenyl)ethenyl]-9*H*-carbazole 19

To a solution of Bu^{t}OK (5.60 g, 0.05 mol) in DMF (40 cm^3) at 75 °C was added a solution of **10b** (0.01 mol) and **11b** (0.01 mol) in DMF (10 cm^3) and the mixture was stirred at this temperature for 18 h. The solution was poured into water (150 cm^3) and the precipitate was filtered. The oily precipitate was chromatographed using light petroleum–EtOAc (9:1) as eluent to give **19**. The fractions which contained not less than 90% of **19** were combined, the solvent evaporated and the residue recrystallized twice from MeOH (20% yield of purified material), mp 151–153 °C.

Hydrolysis of dienamines 14a and 15a: 4-(1-naphthyl)-1-phenylbut-1-en-3-one 22

The dienamine **15a** (0.5 g) was hydrolysed in AcOH–H_2O–HCl (18:1:1 cm^3) by heating under reflux for 7 h. The mixture was poured into H_2O (50 cm^3) and extracted with $CHCl_3$ (3 × 20 cm^3). The $CHCl_3$ layer was washed with saturated aqueous K_2CO_3 (30 cm^3) and H_2O (50 cm^3), dried over $MgSO_4$ and chromatographed twice using light petroleum–EtOAc (94:6). Only repeated extractions with light petroleum removed much of the carbazole. The residual oil contained **22** and carbazole (84:16 estimated by HPLC), ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.3 (s, 2 H, CH_2), 6.77 (d, *J* 16 Hz, 1 H, H1), 7.18–7.53 (m, 10.6 H, aromatic), 7.62 (d, *J* 16 Hz, 1 H, H2), 7.74–8.04 (m, 4 H, aromatic).

The dienamine **14a** (0.5 g) was hydrolysed similarly to give the same mixture.

9-(1-Phenylphenanthren-3-yl)-9*H*-carbazole 23

The dienamine **14a** (0.50 g, 1.2 mmol) was heated in 1,2,4-trichlorobenzene (7.0 g) under reflux for 103 h. After this period the conversion was 88% by HPLC. The solvent was removed by blowing N_2 over the heated solution. The residue was cooled and taken up with $CHCl_3$. The solution was adsorbed on *ca.* 5 g of silica gel and chromatographed over silica gel (30 g) using light petroleum–EtOAc (95:5) as eluent. The fractions which contained over 90% **23** (t_R = 10.2 min) were combined and the solvent evaporated. The residue was boiled in MeOH (30 cm^3) and the volume of solvent reduced to *ca.* 3 cm^3 before filtering. The process of boiling with MeOH, reducing the solvent volume and filtering was repeated twice more. Total material amassed was 0.20 g. This was recrystallized from EtOAc as small needles, mp 227–229 °C.

Technique of thermal equilibration: 14c to 15c and 15c to 14c

In two different test tubes, each containing 1,2,4-trichlorobenzene (2.0 g) and a small stirrer bar, was placed **14c** (0.025 g, 67 μmol) and **15c** (0.010 g, 27 μmol). The two test tubes were each wired to a thermometer so that the bulb was at the level of the liquid in the tubes and this setup was lowered into a silicone oil bath stirring at 180 °C. This temperature was monitored periodically so that any variation did not exceed ±2 °C. The effect of any changes in temperature were largely dampened by the very slow rate of equilibration. Evaporation of solvent is not critical because at 180 °C only a slow evaporation of solvent takes place and, more importantly, the mole fractions at different times [$X_{14c}(t)$], weight fractions (X_{14c}) or peak area (HPLC) fractions [X_{14c}(PA)] being measured are *volume-independent*. The aliquots were taken by dipping an open-ended pasteur pipette into the solution. The small volume that was withdrawn was diluted with methanol (*ca.* 5 cm^3) and the time elapsed was recorded. The methanolic aliquot was injected into the HPLC system and the ratio of peak areas obtained at 300 nm at two different retention times of the same injected sample gives the quantity X_{14c}(PA) from eqn. (1). From stock solutions

$$X_{14c}(\mathrm{PA}) = \mathrm{PA}_{14c}/(\mathrm{PA}_{14c} + \mathrm{PA}_{15c}) \quad (1)$$

of **14c** and **15c**, each 0.0102 g in 1,2,4-trichlorobenzene (2.107 g) (0.013 03 M), a calibration graph was obtained by plotting X_{14c} obtained from the weighed aliquots of **14c** and **15c** diluted with MeOH (*ca.* 5 cm^3) *versus* X_{14c}(PA) [eqn. (1)]. These calibration data are represented by eqn. (2). Using eqn. (2) we evaluate

$$X_{14c} = 0.28149[X_{14c}(\mathrm{PA})]^2 + 0.6924[X_{14c}(\mathrm{PA})] + 0.0101 \quad (2)$$

$X_{14c}(t)$ by substituting the quantity X_{14c}(PA) which was calculated [using eqn. (1)] and from peak areas from HPLC chromatograms of the reaction aliquots taken at different times.¶

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