Synthesis and Properties of *N*-Cyanodimethyltetradehydro-trideca-, -pentadeca-, -heptadeca-, and -nonadeca-azafulvenes, and Benzannelated *N*-Cyanotridecaazafulvene Derivatives

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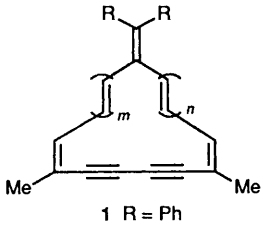
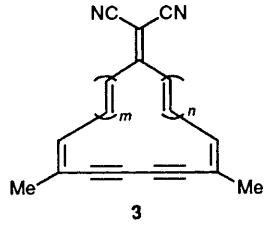
Syntheses of *N*-cyano-5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidenamine, *N*-cyano-5,10-di-*tert*-butylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidenamine, *N*-cyano-7,12-dimethylcyclopentadeca-2,4,6,12,14-pentaene-8,10-diynylidenamine, *N*-cyano-7,12-dimethylcycloheptadeca-2,4,6,12,14,16-hexaene-8,10-diynylidenamine, and *N*-cyano-9,14-dimethylcyclononadeca-2,4,6,8,14,16,18-heptaene-10,12-diynylidenamine are described. Examination of the ^{1}H NMR spectra indicates that the cyclo-C_{13} and cyclo-C_{17} compounds are paratropic, while the C_{15} and C_{19} compounds are diatropic. Syntheses of benzannelated derivatives of the first mentioned annulene, *i.e.* *N*-cyano-11-methyl-12,13,14,15-tetradehydro-7*H*-benzocyclotridecen-7-ylidenamine and *N*-cyano-5,6,7,8-tetradehydro-15*H*-dibenzo[*a*,*g*]cyclotridecen-15-ylidenamine, are also described. Dynamic NMR analysis of the ring protons suggested a *syn–anti* isomerization of the cyano group at the exocyclic position of the macrocycle. The influence of the cyanoimino group and benzannelation upon the tropicity of the tetradehydro[13]annulenes is discussed on the basis of their ^{1}H NMR and electronic spectra.

Recently we have investigated cyclic cross-conjugated systems of ring-expanded fulvalenes[1] and fulvenes derived from the tetradehydroannulenones.[2] Of these, the diphenylmethylene-**1**[3] and the dichloromethylenetetradehydroannulene derivatives **2**[4] proved to be atropric, reflecting the absence of any cross-conjugation of π-electrons, or any contribution from a dipolar structure in the ground state. In contrast, the dicyanomethylenetetradehydroannulene derivatives **3** proved to show a ring-current effect, reflecting the presence of a contribution from a dipolar structure **3a** in the ground state.[5]



1 R = Ph
2 R = Cl



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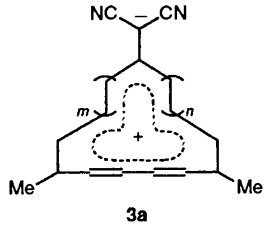


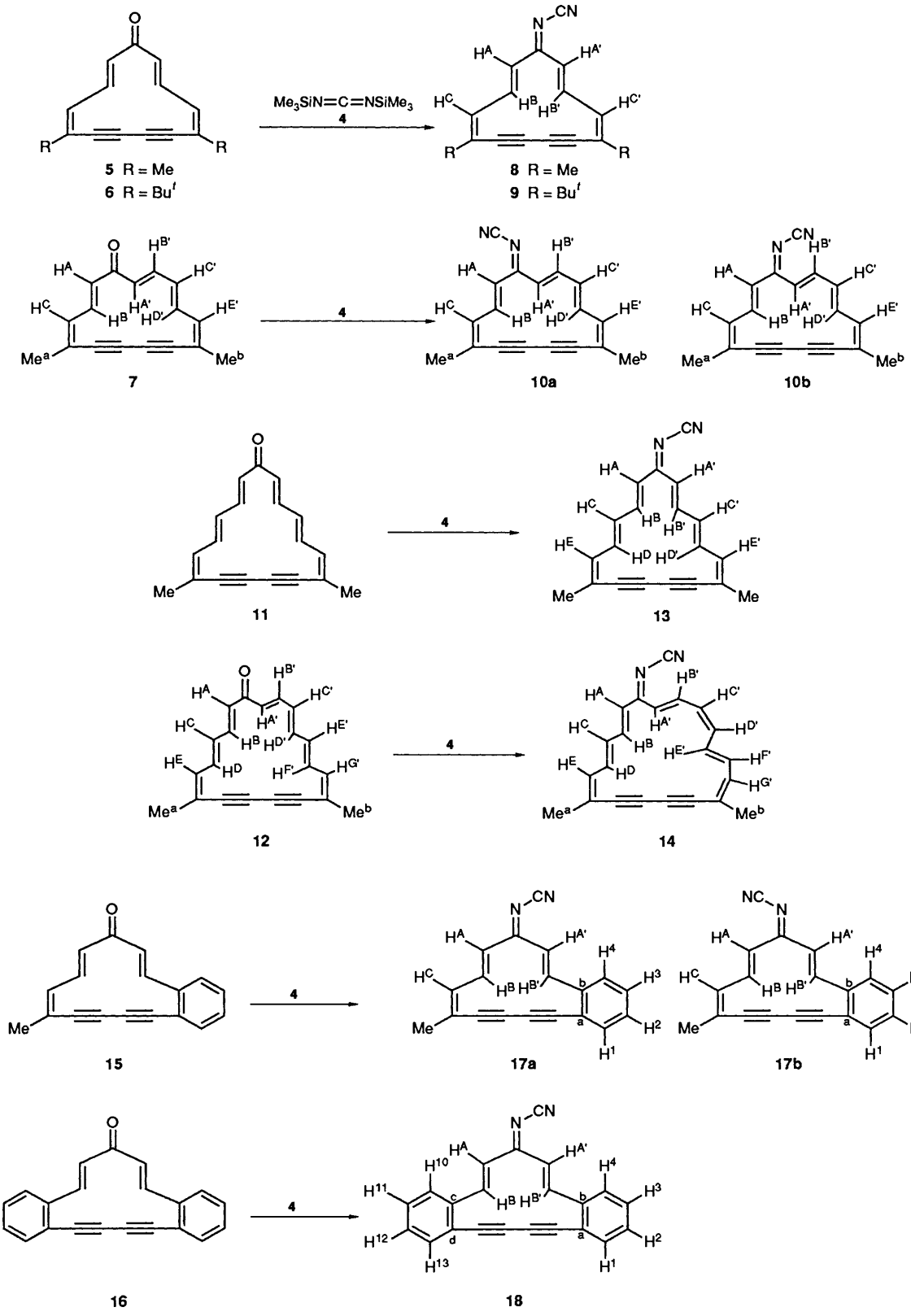
3a

In our continuing effort to search for two-dimensional, π-electron conjugated compounds for nonlinear optical behaviour,[6] we expected that *N*-cyanoiminotetradehydroannulene derivatives **8**–**10**, **13** and **14** with a strongly electron-withdrawing cyanoimino group at the exocyclic position would show a larger ring-current effect than do the corresponding tetradehydroannulenones **5**–**7**, **11** and **12** and the dicyanomethyleneannulenes **3**. We have now realized this expectation in practice. Also, the effect of benzannelation to lower the tropicity of the macrocyclic azafulvene system was confirmed from examination of the monobenz- **17** and the dibenzannelated derivatives **18** of the [13]annulene. This paper deals with syntheses and properties of the title compounds **8**–**10**, **13**, **14**, **17** and **18**,[7] of which the *N*-cyanoiminoannulenes **8**–**10**, **13** and **14** are the first examples of azafulvenes containing a large monocyclic ring to show a ring-current effect.[8]

The annulenes prepared in this study show broadening and coalescence of the ring-proton signals in the range 70–100 °C, suggesting *syn–anti* isomerization of the cyano group at the exocyclic position of the macrocycles. Dynamic NMR analyses were performed to obtain the energy barrier for this isomerization.

Results and Discussion

Synthesis.—Recently, Iwatsuki *et al.*,[9] and Bryce and Davies[10] have reported the preparation of several cyanoquinomethanimines, in which the carbonyl group of quinones was replaced by the cyanoimino group. The method employs a titanium tetrachloride-mediated reaction with bis(trimethylsilyl)carbodiimide **4**.[11] We have now successfully applied this method to the synthesis of the title compounds by using the tetradehydroannulenones **5**–**7**, **11**, **12**, **15** and **16**, which are now relatively readily available,[1–5,12,13] as the starting materials. Reaction of dimethyltetradehydro[13]annulenone **5**,[2a] di-*tert*-butyltetradehydro[13]annulenone **6**,[12] dimethyltetradehydro[15]annulenone **7**,[2b] dimethyltetradehydro[17]annulenone **11**,[2b] dimethyltetradehydro[19]annulenone **12**,[2b] methyltetradehydrobenz[13]annulenone **15**,[13] and tetradehydrodibenz[13]-



annulenone **16**[13] with a large excess of bis(trimethylsilyl)-carbodiimide **4**[11] in the presence of titanium tetrachloride in dry benzene at room temperature gave *N*-cyano-5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidenamine **8** (55%), *N*-cyano-5,10-di-*tert*-butylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidenamine **9** (82%), *N*-cyano-7,12-dimethylcyclopentadeca-2,4,6,12,14-pentaene-8,10-diynylidenamines **10** (27%), *N*-cyano-7,12-dimethylcycloheptadeca-2,4,6,12,14,16-hexaene-8,10-diynylidenamine **13** (45%), *N*-cyano-9,14-dimethylcyclononadeca-2,4,6,8,14,16,18-heptaene-10,12-diynylidenamine **14** (26%), *N*-cyano-11-methyl-12,13,14,15-tetradehydro-7*H*-benzocyclotridecen-7-ylidenamines **17** (60%), and *N*-cyano-5,6,7,8-tetradehydro-15*H*-dibenzo[*a*,*g*]cyclotridecen-15-ylidenamine **18** (38%), respectively. These *N*-cyanoiminoannulenes **8**–**10**, **13**, **14**, **17** and **18** gave satisfactory elemental analyses except for the [19]annulene **14**, and they were obtained as coloured crystals and proved to be thermally unstable and sensitive to diffused light and air. Also, they were susceptible to hydrolysis with even

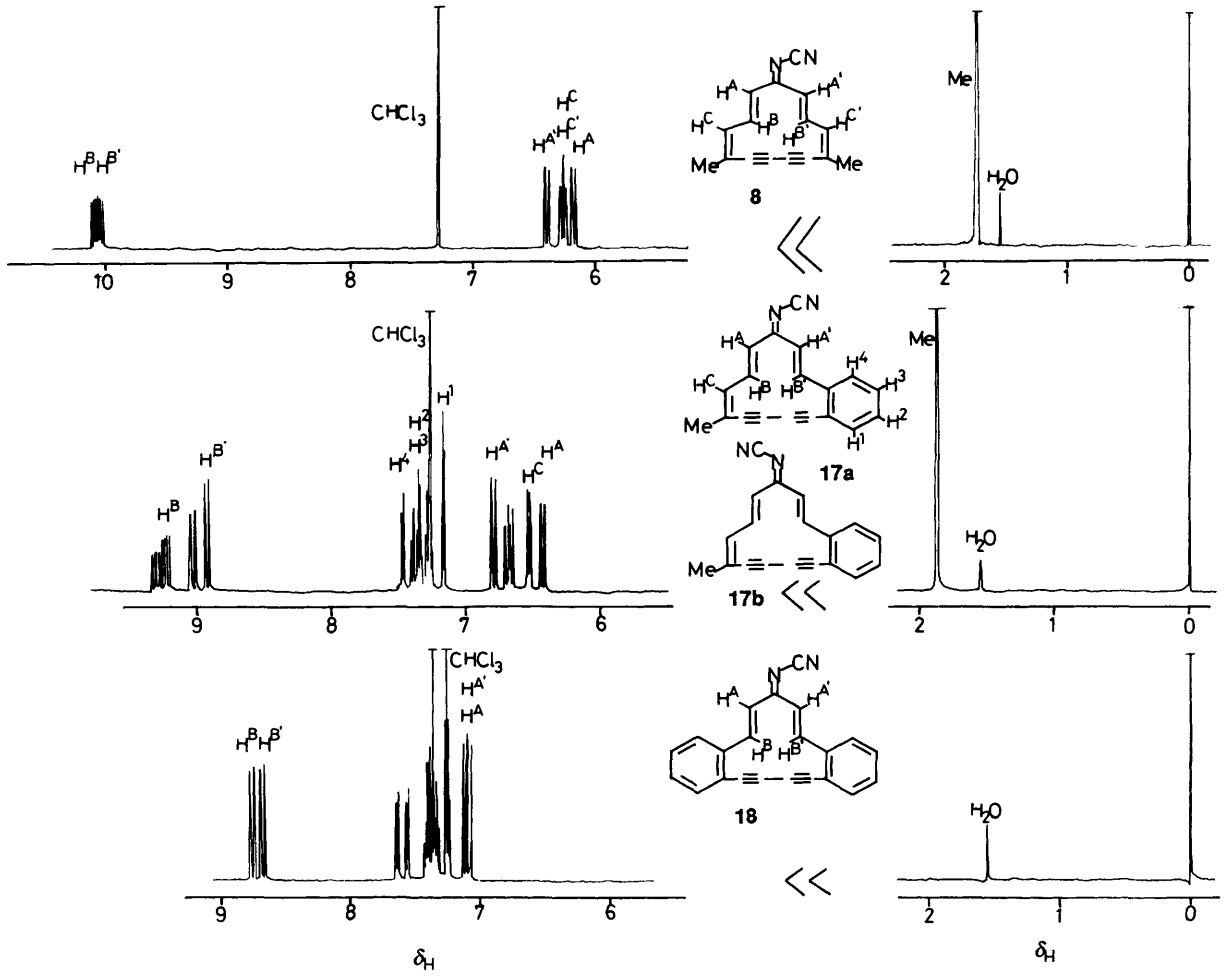


Fig. 1 500 MHz ^{1}H NMR spectra of compounds **8**, **17** and **18** (in $CDCl_3$) at room temperature. In the spectrum of compound **17** the assignments are made for isomer **17a**.

a trace of water in solution, and reverted to the respective starting tetradehydroannulenones **5**–**7**, **11**, **12**, **15** and **16** on storage even at low temperature.

The ^{1}H *NMR Spectra and the Geometrical Determination.*— Chemical-shift assignments of the olefinic protons were made as follows. Broad doublet signals were assigned to the terminal protons of the polyene chain adjacent to the methyl groups, because the broadening can be ascribed to allylic coupling to the methyl protons, while sharp doublets are assigned to the protons adjacent to the cyanoimino group. The protons adjacent to the terminal protons are then usually detected by decoupling experiments, and in turn the protons adjacent to these protons are found, and so on. Geometries were deduced by using the magnitudes of the coupling constants; 14–16 Hz for a *trans* (*E*) double bond, 9–11 Hz for a *cis* (*Z*) double bond, 10–12 Hz for an *s-trans* single bond between two double bonds, and 5–7 for an *s-cis* single bond.[14]

The ^{1}H NMR spectra of compounds **8**, **17**, **18**, and those of **9**, **10**, **13** and **14** taken at room temperature are presented in Figs. 1 and 2, respectively, and the spectra of the olefinic protons in compound **10** are shown in Fig. 3. The chemical shifts and the coupling constants are listed in Table 1. The chemical-shift data of the ^{13}C NMR spectra are given in the Experimental section.

The structures of the [13]annulenes, **8** and **9**, were unambiguously deduced as shown with a symmetrical skeleton from the coupling constants given in Table 1. The chemical-shift assignments were based on the assumption that the $H^{A'}$ proton close to the cyano group would appear at a lower field than would the H^A proton because of the magnetic anisotropy effect of the cyano group.[15]

The ^{1}H NMR spectrum (Fig. 2) of the [15]annulene **10** revealed that the compound exists as a mixture of two isomers which have the same skeletal geometry but differ in the orientation of the cyano group, **10a** and **10b**, in an equilibrium ratio of 7:3. The coupling-constant data for the major isomer suggested that the diene moiety ($-CH^A{=}CH^B{-}CH^C{=}$) had a *trans–s–trans* geometry and the triene moiety ($-CH^{A'}{=}CH^{B'}{-}CH^{C'}{=}CH^{D'}{-}CH^{E'}{=}$) had a *trans–s-cis–trans–s-trans* geometry. The skeletal geometry is therefore the same as that in the corresponding annulenone **7**, which was reported previously[2b] and reconfirmed recently by 500 MHz ^{1}H NMR spectroscopy (see the Experimental section). The same geometry was assigned to the minor isomer although some of the coupling constants could not be precisely read. Structure **10a** was assigned to the major isomer because the signals assigned to H^A and $H^{B'}$ resonated at a lower field and at a higher field, respectively, than did the corresponding protons in the other isomer. Predominance of isomer **10a** can be ascribed to the smaller steric interaction of the cyano group with H^A in **10a** than with $H^{A'}$ in **10b**. As described in detail later, the interconversion between these isomers takes places on the NMR time-scale at higher temperatures.

The ^{1}H NMR data (Fig. 2 and Table 1) of the [17]annulene **13** showed that both of the triene moieties have a *trans–s-trans–trans–s-trans* geometry, indicating a symmetrical structure for the macrocyclic skeleton. The downfield signal assigned to the

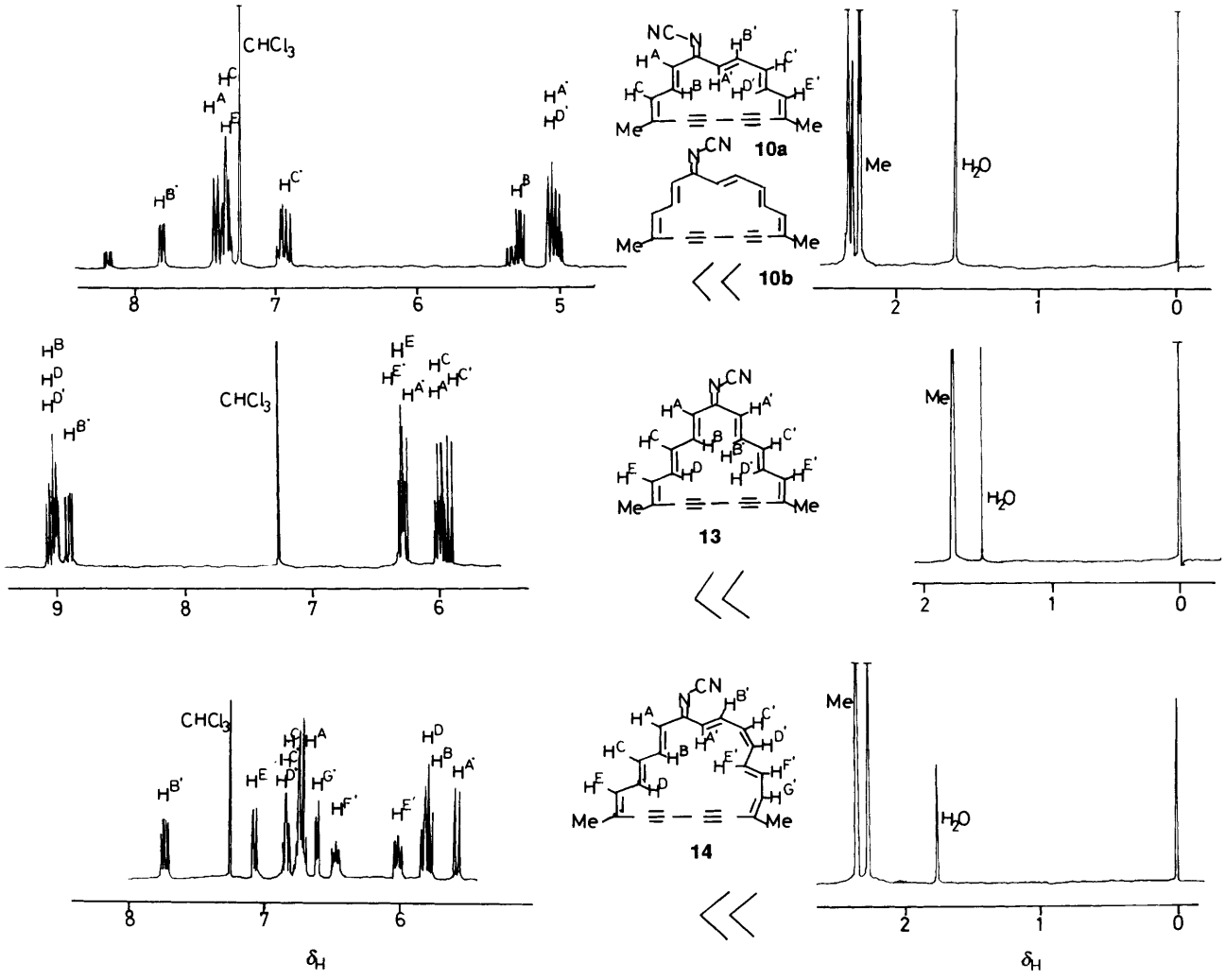


Fig. 2 500 MHz ^{1}H NMR spectra of compounds **10**, **13** and **14** (in $CDCl_3$) at room temperature. In the spectrum of compound **10** the assignments are made for isomer **10a**.

protons adjacent to the cyanoimino group was ascribed to $H^{A'}$, taking the anisotropy effect of the cyano group into account.

The structure of the [19]annulene **14** is somewhat puzzling. The coupling-constant data suggested that the triene moiety was *trans–s-trans–trans–s-trans*, and that the tetraene moiety was *trans–s-cis–cis–s-trans–trans–s-cis*. The geometry in the tetraene moiety is therefore quite different from that in the corresponding annulenone **12** reported before,[2b] in which the tetraene chain had been deduced to have a *trans–s-cis–trans–s-trans–trans–s-trans* geometry. We reexamined the ^{1}H NMR spectrum of compound **12** at 500 MHz and confirmed the previous assignments (see the Experimental section). The spectral data indicated that the macrocyclic ring in compound **12** maintained considerable rigidity and planarity. In contrast, the ring in compound **14** seemed rather flexible and nonplanar, especially in the tetraene moiety, as judged from the somewhat broadened signals for $H^{E'}$ and $H^{F'}$ (Fig. 2) and the magnitude of the coupling constants $J_{D'E'}$ and $J_{F'G'}$ (Table 1). Although the reason for the change in the skeletal geomtry is not clear, this behaviour was not observed in the corresponding carbocyclic fulvalenes [1] and the carbofulvene systems **1** and **2**.[3,4]

The orientation of the cyano group in compound **14** was assigned *syn* to the tetraene moiety as follows. The chemical shift of H^A in compound **14** (δ 6.73) was closer to that in isomer **10b** (δ 6.92) than to that in isomer **10a** (δ 7.43), suggesting that H^A in compound **14** is *anti* to the cyano group. The direct comparison of the chemical shift of $H^{B'}$ with the corresponding protons in isomers **10a** and **10b** might be fraught with difficulty because the rigidity and planarity of the moieties around $H^{B'}$ are considerably different between species **10** and **14** and thus the effect of tropicity on the chemical shifts may be different. The average of the chemical shifts of $H^{A'}$ and $H^{B'}$ can cancel out the tropicity effect and can be a measure of the anisotropy effect of the cyano group. The values are δ 6.66, 6.44 and 6.59 for compounds **14**, **10a** and **10b**, respectively. Therefore the anisotropy effect in compound **14** was similar to that in compound **10b**, supporting the assignments of the cyano orientation. The steric interaction of the cyano group with $H^{A'}$ in this isomer may be smaller than that with H^A in the other possible isomer with the opposite orientation for the cyano group, because the latter interaction occurs in-plane while the former out-of-plane.

The monobenzannelated compound **17** exists in two isomers **17a** and **17b** in an equilibrium ratio of 5:4 in $CDCl_3$. The assignments were again based on the anisotropy effect of the cyano group and the major isomer was assigned to structure **17a**.

As is seen from Figs. 1 and 2, and Table 1, the methyl protons of compounds **8** and **13** resonate at a high field of $\delta \sim 1.7$ and the olefinic outer protons of compounds **8**, **9** and **13** appear at higher field than do the inner protons. Therefore, the compounds **8**, **9** and **13** are paratropic, in which the macrocyclic moieties behave as 12π- and 16π-electron systems, respectively, owing to polarization of the C=N bond. Conversely, the methyl

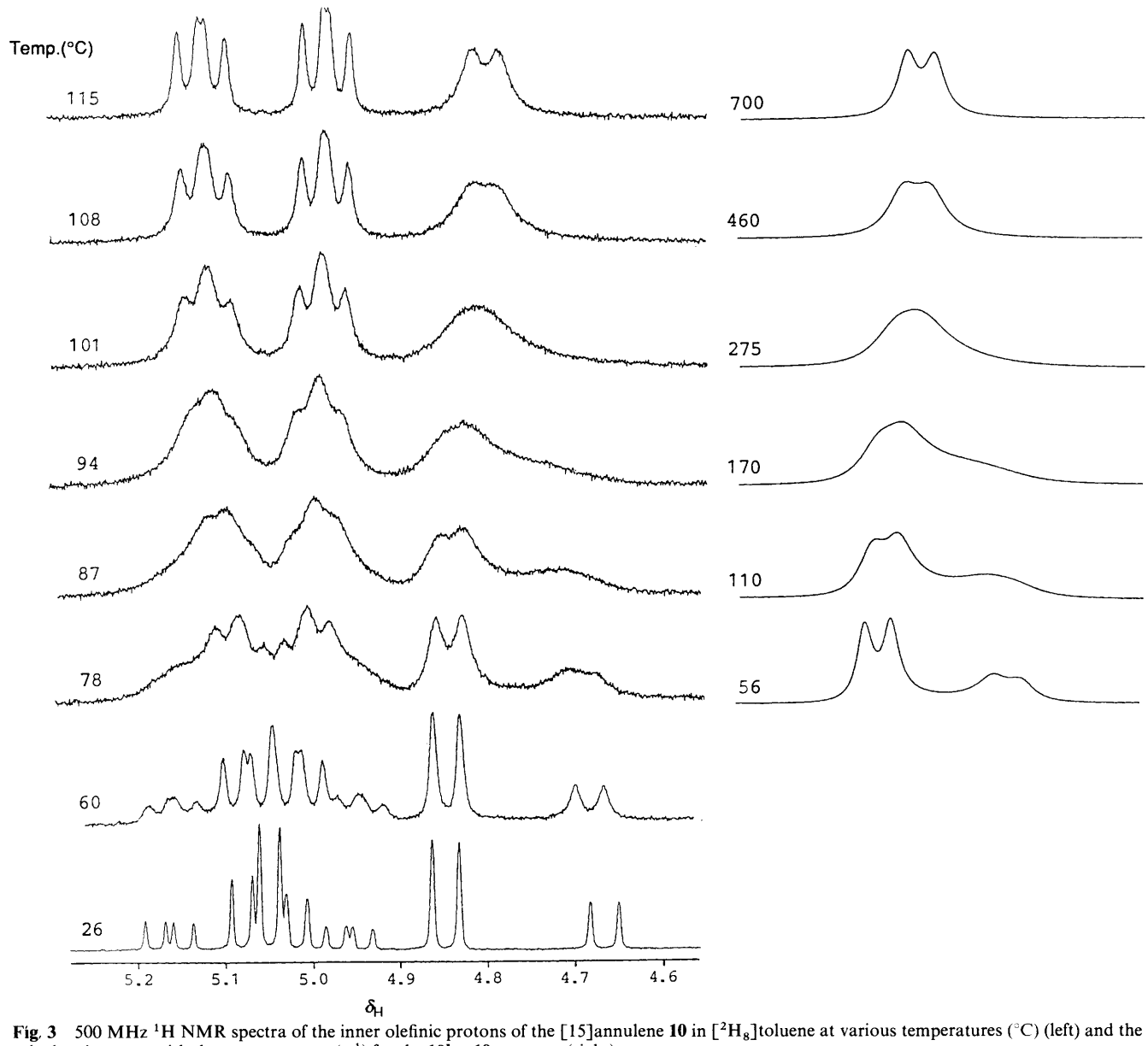


Fig. 3 500 MHz ^{1}H NMR spectra of the inner olefinic protons of the [15]annulene **10** in [$^2H_8$]toluene at various temperatures (°C) (left) and the calculated spectra with the rate constants (s^{-1}) for the **10b**→**10a** process (right)

protons of the compounds **10** and **14** resonate at lower field, $\delta \sim 2.3$, and the olefinic outer protons appear at a lower field than the inner protons, indicating that the compounds **10** and **14** are diatropic, as expected for 14π- and 18π-electron systems, respectively. The chemical shifts of the olefinic protons of compounds **17** and **18** suggested the monobenzannelated compound **17** to be weakly paratropic and the dibenzannelated one **18** to be atropic (Fig. 1), indicating that the tropicity falls off in the sequence **8** > **17** > **18**, *i.e.* with increasing number of fused benzene rings on the tetradehydro[13]annulene system, as has been demonstrated for the dicyanoannulenes **3**,[5] dehydroannulenones **5**, **15**, **16**,[13] and dehydroannulene systems.[16] Therefore, although it is predicted that the local anisotropy of a 1,3-diacetylenic linkage in compounds **8** and **17** will also shift the inner-proton resonances considerably downfield,[17] the fact that the low-field shifts of the inner-proton resonances in the [13]annulene series decrease upon benzannelation shows that the shifts observed in compounds **8** and **17** are in part attributed to a paramagnetic ring current,[18] *i.e.*, compounds **8** and **17** are really paratropic as described above.

The chemical-shift differences $\Delta\delta$ between the inner and the outer olefinic protons are regarded as an experimental measure of the ring-current effect.[15,19] The values for compounds **8**, **10**, **13** and **14** are listed in Table 2, together with those for the dicyanoannulenes **3** and the tetradehydroannulenones **5**, **7**, **11** and **12**. For comparison among these compounds the chemical shifts of the farthest olefinic inner and outer protons of the macrocycles from the exocyclic moiety, *i.e.* the inner protons at β-positions and the outer protons at α-positions to the methyl group, were chosen in order to minimize possible anisotropy and electric-field effects due to the exocyclic moiety. As is seen from Table 2, among compounds with the same ring size the *N*-cyanoiminoannulenes show the largest chemical-shift difference and the tetradehydroannulenones the smallest. This is in accord with a decreasing order of electron-withdrawing effect of the substituent at the exocyclic position. Therefore, the *N*-cyanoiminoannulenes show larger tropicity than do the tetradehydroannulenones **5**, **7**, **11** and **12** and the dicyanoannulenes **3**, due to a combination of the inductive, electron-withdrawing effect of the cyano group and the large electronegativity of the nitrogen atom.

Table 1 ^{1}H NMR data of the compounds **8**, **9**, **10a**, **10b**, **13**, **14**, **17a**, **17b** and **18** (in $CDCl_3$) at 500 MHz, determined at room temperature

	δ_H(*J*/Hz)															
Compound	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	$H^{F'}$	$H^{G'}$	H^1	H^2	H^3	H^4	Me
8	6.38d (16.5)	6.16d (16.5)	10.07dd (16.5, 10)	10.04dd (16.5, 10)	6.26d (10)	6.23d (10)											1.75, 1.74
9	6.02d (16.5)	6.38d (16)	10.27dd (16.5, 10)	10.13dd (16, 9.5)	6.22d (10)	6.24d (9.5)											1.07[a]
10a	7.43d (15.5)	5.07d (15)	5.28dd (15.5, 11.5)	7.81dd (15.5, 5)	7.35d (11.5)	6.95dd (15.5, 5)		5.03dd (15.5, 12)		7.37d (12)							2.34,[b] 2.25[c]
10b	6.92d[d]	5.00d (16)	5.34dd (16, 11.5)	8.19dd (16, 5.5)	7.33d[d]	6.98dd[d]		5.05[d]		7.35d[d]							2.31,[b] 2.24[c]
13	5.91d (16)	6.27d (15.5)	9.05dd (16, 11)	8.90dd (15.5, 11)	6.01dd (15, 11)	5.98dd (15, 11)	9.03dd (15, 11.5)	9.00dd (15, 11.5)	6.29d (11.5)	6.31d (11.5)							1.76[e]
14	6.73d (15)	5.59d (15.5)	5.79dd (15, 12.5)	7.73dd (15.5, 6.5)	6.72dd (15, 12.5)	6.75dd (11, 6.5)	5.82dd (15, 11.5)	6.85t (11)	7.07d (11.5)	6.02dd (15.5, 11)	6.48dd (15.5, 8.5)	6.62d (8.5)					2.36,[c] 2.27[b]
17a	6.43d (16.5)	6.79d (16.5)	9.22dd (16.5, 10.5)	8.92d (16.5)	6.53d (10.5)								7.16d (7.5)	7.29dt (7.5, 1)	7.35t (7.5)	7.47d (7.5)	1.88
17b	6.69d (16)	6.67d (16.5)	9.30dd (16, 10.5)	9.02d (16.5)	6.53d (10.5)								7.16d (7.5)	7.26dt (7.5, 1)	7.34t (7.5)	7.39d (7.5)	1.88
18	7.09d (16.5)	7.11d (16.5)	8.74d (16.5)	8.66d (16.5)									7.24d (7.5)	7.35dt (7.5, 1)	7.40t (7.5)	7.63d (7.5)	
													H^{10} 7.55d (7.5)	H^{11} 7.39t (7.5)	H^{12} 7.33dt (7.5, 1)	H^{13} 7.25d (7.5)	

[a] *tert*-Butyl protons. Accidentally isochronous. [b] Me^a protons. [c] Me^b protons. [d] Coupling constants could not be read because of signal overlap. [e] The two methyl groups are isochronous.

Table 2 The chemical-shift differences ($\Delta\delta = \delta_i - \delta_o$) between the inner (i) and outer (o) olefinic protons of tetradehydroannulenones, dicyanofulvenes **3**, and *N*-cyanoiminoannulenes[a]

Ring size	Tetradehydroannulenones[b]	Δδ/ppm Dicyanoannulenes **3**[c]		*N*-Cyanoiminoannulenes	
[13]-	**5** 3.10	*m* = *n* = 1	3.48	**8**	3.79
[15]-	**7** −1.51	*m* = 1, *n* = 2	−1.54	**10**	−2.21[d]
[17]-	**11** 2.30	m = n = 2	2.47	**13**	2.72
[19]-	**12** −1.15			**14**	−1.25[e]

[a] δ_i and δ_o are the average values between the inner β and the outer α protons to the methyl groups, respectively. [b] Ref. 2(*b*) and Experimental section. [c] Ref. 5(*b*). [d] The value for isomer **10a**. [e] The value from the chemical shifts of the protons H^D and H^E.

Table 3 Kinetic parameters for *syn–anti* isomerization

Compound	$\Delta H^{\ddagger}$ kcal mol^{-1}[a]	$\Delta S^{\ddagger}$ cal mol^{-1}[a]	$\Delta G^{\ddagger}_{350K}$ kcal mol^{-1}[a]
8	19.0 ± 0.4	0.7 ± 1.1	18.7
9	19.2 ± 1.2	1.7 ± 3.2	18.6
17, **17a** ⟶ **17b**	19.7 ± 0.3	3.4 ± 0.7	18.5
17b ⟶ **17a**	20.2 ± 0.3	5.1 ± 0.8	18.3
18	18.7 ± 0.5	0.9 ± 1.3	18.4
10, **10a** ⟶ **10b**	17.8 ± 0.8	−0.3 ± 2.0	17.8
10b ⟶ **10a**	17.1 ± 0.8	−0.8 ± 2.0	17.3
13	19.2 ± 0.3	1.0 ± 0.9	18.8

[a] 1 cal = 4.184 J.

The syn–anti Isomerization of the Cyano Groups.—As shown above, two isomers in compounds **10** and **17** are separately detected by NMR spectroscopy at room temperature and therefore the configurational change at nitrogen is slow on the NMR time-scale; and so is it in compounds **8**, **9**, **13** and **18**, although only one isomer is present in these compounds. However, it was found that the configurational change at nitrogen, *i.e.*, *syn–anti* isomerization of the cyanoimino group, takes place on the NMR time-scale at elevated temperatures in all of these compounds. Hence, in [$^2H_8$]toluene, the lineshape of the olefinic proton signals was dependent on the temperature. As a typical example, the ^{1}H NMR spectra of the inner olefinic protons of compound **10** at various temperatures are shown in Fig. 3. The $H^{A'}$ proton gave two definite doublets at δ 4.85 and 4.67 due to isomers **10a** and **10b**, respectively, at 26 °C in the intensity ratio of 2.3:1. On elevation of the temperature these signals broadened and coalesced into a doublet, reflecting the increasing rate of the **10a** ⇌ **10b** interconversion by *syn–anti* isomerization of the cyanoimino group. Similarly, two pairs of double doublets at δ 5.2–4.9 assigned to H^B and $H^{D'}$ also broadened and coalesced into two double doublets upon increasing the temperature. Lineshape analysis of the $H^{A'}$ signals at several temperatures gave the rate constants for the isomerization at the respective temperatures. The activation parameters obtained therefrom are shown in Table 3 together with those obtained for the other compounds.

Syn–anti isomerization of the imino group has been well studied in a variety of imino-containing compounds and has been found to occur either by inversion at nitrogen or by rotation about the C=N double bond.[20] The mechanism depends on the nature of the substituents attached to the imino group. The energy barriers, either to inversion or to rotation, suffer from many factors, electronic and steric.

In the present cases the $\Delta H^{\ddagger}$- and $\Delta G^{\ddagger}$-values do not significantly change among the compounds examined and therefore it may be unwise to discuss the barrier height differences in terms of a single factor. However, the somewhat lower barriers in compound **10** than in the other compounds can be ascribed to the larger polarization of the C=N bond in compound **10** due to the aromatic stabilization of the macrocyclic moiety. The fact that compound **10** shows the lowest C=N stretching frequency (1605 cm^{-1}) among the compounds may also be a reflection of this situation.

No definite conclusion can be drawn as to the mechanism of the isomerization. The feature mentioned above seems to favour the rotational mechanism but the inversion mechanism cannot be excluded because polarization of the C=N bond will also decrease the inversion barrier.

Electronic Spectra.—The electronic absorption maxima of compounds **8–10**, **13**, **14**, **17** and **18**, determined in both tetrahydrofuran (THF) and acetonitrile, are listed in Table 4. It is evident from Table 4 that all the bands of compounds **8–10**, **13**, **14**, **17** and **18** show a small hypsochromic shift on changing the solvent from less polar THF to polar acetonitrile. This solvent effect strongly supports the interpretation that a π-electron polarization from the macrocycles to the exocyclic moiety, as depicted in structure **3a**, occurs in these systems.

In the spectra of the [13]annulene series, the main maxima shifted to longer wavelengths in the sequence non-benzannelated **8** < monobenzannelated **17** < dibenzannelated **18**, indicating that fusion of benzene rings results in an appreciable bathochromic shift, as has been recognized for carbocyclic benzannulene series.[21]

The absorption curves of compounds **8** and **13**, and those of compounds **10** and **14**, are similar, and differ only in the bathochromic shift of each band.

Table 4 shows that the main maximum of the [15]annulene **10** is at longer wavelength than that of the next higher homologue, the [17]annulene **13** and that the main maxima of the [4*n* + 3]annulenes **10** and **14** are at considerably longer wavelengths. Therefore it is evident that in these *N*-cyanoiminoannulenes the same alternation in the wavelengths of the main electronic absorption maxima between [4*n* + 2] and [4*n*] systems occurs, as has already been demonstrated for monocyclic annulenes, dehydroannulenes,[22] and the dicyanoannulenes **3**.[5]

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a Hitachi 260-50 spectrophotometer as KBr discs and were calibrated against polystyrene; only significant maxima are described. Electronic spectra were measured in THF and acetonitrile solutions, and run with a Hitachi 220A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions with a Bruker AM-500 spectrometer at 500.14 and 125.76 MHz, respectively, $SiMe_4$ being used as internal standard. *J*-Values are given in Hz. The ^{1}H NMR assignments were clarified by the use of decoupling experiments. Variable-temperature ^{1}H

Table 4 Electronic absorption maxima of the compounds **8**–**10**, **13**, **14**, **17** and **18** [a, in THF, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}); b, in acetonitrile, λ_{max} (relative extinction coefficients)]. Strongest absorptions are indicated in bold type.

8	a	242 (10 900), 255sh (13 000), 278sh (26 800), **291** (**32 600**), 338 (15 100)
	b	240 (0.33), 255sh (0.39), 277sh (0.83), 289 (1.00), 335 (0.47)
17	a	264 (19 600), **297** (**36 900**), 357sh (10 500), 435 (2 000)
	b	260 (0.51), 296 (1.00), 351sh (0.31), 434 (0.07)
18	a	264sh (16 900), 296sh (33 500), **308** (**44 900**), 353sh (10 300)
	b	256 (0.33), 294sh (0.73), 307 (1.00), 350sh (0.22)
9	a	241 (12 500), 256sh (15 600), 278sh (30 900), **290** (**37 200**), 338 (18 400)
	b	239 (0.34), 254sh (0.41), 275sh (0.80), 288 (1.00), 338 (0.50)
10	a	253 (23 500), 258 (23 700), 275sh (23 100), **327** (**36 000**), 445 (11 700)
	b	275 (0.68), 325 (1.00), 444 (0.29)
13	a	235 (13 100), 274 (24 400), 296sh (30 700), **314** (**49 000**), 326sh (47 700), 375 (18 700)
	b	273 (0.44), 294sh (0.69), 313 (1.00), 325sh (0.95), 374 (0.43)
14	a	266sh (23 000), 280 (23 700), **346** (**42 000**), 430sh (12 700)
	b	275sh (0.40), 344 (1.00), 427sh (0.34)

NMR measurements were made on the AM-500 in [$^2H_8$]-toluene and the temperatures were calibrated with an ethylene glycol sample.

Total lineshape analysis was made by use of the DNMR3 program.[23] The olefinic proton signals that were located at the highest or lowest field and were not disturbed by other signals were chosen for the analysis and were analysed as the X part of an AX or ABX spin system. Spectra obtained at six or seven temperatures in the 70–115 °C range were simulated and rate constants were determined. The temperature dependence of the chemical-shift differences and the T_2-values, as well as of the isomer populations where necessary, were properly taken into account. Least-squares analysis of the obtained rate constants gave the kinetic parameters given in Table 3.

All the reactions were carried out at room temperature under argon. Merck alumina (activity II–III) and Merck silica gel 60 were used for column chromatography. Compounds were preadsorbed from hexane, diethyl ether, or benzene solution onto the adsorbent before column chromatography. Progress of all reactions was followed by TLC on Merck precoated silica gel. Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulphate prior to removal of solvent. Solvents were evaporated under water-pump pressure.

The ^{1}H *and* ^{13}C *NMR Data of the Tetradehydro*[15]*annulenone* **7**.[2b]—δ_H 7.54 (1 H, dd, *J* 15.5 and 5, $H^{B'}$), 7.22 (1 H, br d, *J* 12, $H^{E'}$), 7.20 (1 H, br d, *J* 11.5, H^C), 6.81 (1 H, dd, *J* 15.5 and 5, $H^{C'}$), 6.63 (1 H, d, *J* 16.5, H^A), 5.83 (1 H, dd, *J* 16.5 and 11.5, H^B), 5.63 (1 H, d, *J* 15.5, $H^{A'}$), 5.46 (1 H, dd, *J* 15.5 and 12, $H^{D'}$), 2.24 (3 H, s, Me[a]) and 2.18 (3 H, s, Me[b]); see also ref. 2*b*; δ_C 191.1 (C-1), 142.0 (C-14: C–H^B), 140.6 (C-6), 138.9 (C-13: C–H^C), 138.7 (C-3), 134.0 (C-5), 132.9 (C-15: C–H^A), 129.3 (C-7 or -12), 128.6 (C-4), 126.3 (C-2), 123.9 (C-12 or -7), 91.2 (C-9 or -10), 88.7 (C-10 or -9), 84.7 (C-8 or -11), 84.1 (C-11 or -8), 21.6 (12-Me) and 20.8 (7-Me).

The ^{1}H *and* ^{13}C *NMR Data of the Tetradehydro*[19]*annulenone* **12**.[2b]—δ_H 7.00 (1 H, d, *J* 11.5, $H^{G'}$), 6.97 (1 H, d, *J* 12, H^E), 6.95 (1 H, dd, *J* 16 and 6.5, $H^{B'}$), 6.88 (1 H, dd, *J* 14.5 and 11, H^C), 6.81 (1 H, dd, *J* 14.5 and 11, $H^{E'}$), 6.64 (1 H, dd, *J* 15 and 6.5, $H^{C'}$), 6.44 (1 H, d, *J* 16, H^A), 6.18 (1 H, d, *J* 16, $H^{A'}$), 6.00 (1 H, dd, *J* 16 and 11, H^B), 5.86 (1 H, dd, *J* 14.5 and 12, H^D), 5.81 (1 H, dd, *J* 14.5 and 11.5, $H^{F'}$), 5.61 (1 H, dd, *J* 15 and 11, $H^{D'}$), 2.17 (3 H, s, Me[a]) and 2.13 (3 H, s, Me[b]); see also ref. 2*b*; δ_C 193.1 (C-1: C=O), 147.2 (C-18: C–H^B), 141.3 (C-3), 140.7 (C-16: C–H^D), 140.4 (C-5), 139.6 (C-8), 138.6 (C-15: C–H^E), 138.1 (C-7), 131.1 (C-19: C–H^A), 129.7 (C-6), 129.7 (C-17: C–H^C), 128.1 (C-4), 127.2 (C-2), 124.9 (C-9 or -14), 122.5 (C-14 or -9), 86.1 (C-11 or -12), 84.6 (C-12 or -11), 82.7 (C-10), 82.7 (C-13), 22.3 (14-Me) and 21.4 (9-Me).

N-*Cyano*-5,10-*dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidenamine* **8**.—To a stirred solution of dimethyltetradehydro[13]annulenone **5**[2a] (500 mg, 2.40 mmol) in dry benzene (57 cm^3) was added dropwise a solution of titanium tetrachloride (1.28 cm^3, 12.1 mmol) in dry benzene (17 cm^3) during 1.5 h under argon at room temperature. Then a solution of bis(trimethylsilyl)carbodiimide **4**[11] (2.25 g, 12.1 mmol) in dry benzene (17 cm^3) was added dropwise to the mixture during 2 h at room temperature. After being stirred for 17 h at room temperature the mixture was poured onto water and the aqueous layer was extracted with benzene. The combined extracts were washed with aq. sodium hydrogen carbonate and dried. The residual red liquid obtained after removal of solvent was chromatographed on silica gel (3.3 × 9.7 cm). The fractions eluted with hexane–benzene (1:4) afforded the *tetradehydro*[13]*annulene* **8** (306 mg, 55%). It formed brown needles, m.p. 184–186 °C (decomp.) (from hexane–benzene); *m*/*z* 232 (M^+, 64%) and 190 (100); M, 232.2; for UV data see Table 4; ν_{max}/cm^{-1} 2170 (C≡N), 2110 (C≡C), 1630 (C=N), 1600 (C=C) and 990 (*E*-HC=CH); for ^{1}H NMR data see Tables 1 and 3, Fig. 1; δ_C 185.0 (C-1: C=N), 145.4 (C-12: C–H^B), 144.4 (C-3), 140.1 (C-11: C–H^C), 139.7 (C-4), 130.6 (C-5 or -10), 128.7 (C-10 or -5), 128.0 (C-13: C–H^A), 123.8 (C-2), 114.1 (C≡N), 99.7 (C-7 or -8), 99.1 (C-8 or -7), 87.5 (C-6 or -9), 86.5 (C-9 or -6), 20.1 (Me) and 20.0 (Me) (Found: C, 82.45; H, 5.3; N, 11.7. $C_{16}H_{12}N_2$ requires C, 82.7; H, 5.2; N, 12.1%).

N-*Cyano*-5,10-*di*-tert-*butylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidenamine* **9**.—To a stirred solution of di-*tert*-butyltetradehydro[13]annulenone **6**[12] (533 mg, 1.82 mmol) in dry benzene (45 cm^3) was added dropwise a solution of titanium tetrachloride (0.97 cm^3, 9.19 mmol) in dry benzene (13 cm^3) during 1 h. Then a solution of compound **4** (1.70 g, 9.19 mmol) in dry benzene (13 cm^3) was added dropwise to the mixture during 2 h. After being stirred for 2.5 h the mixture was worked up as for the isolation of compound **8**. The product was chromatographed on silica gel (3.2 × 12 cm). The fractions eluted with hexane–benzene (1:4) afforded the *di*-tert-*butyltetradehydro*[13]*annulene* **9** (474 mg, 82%). It formed brown needles, m.p. 216–218 °C (decomp.) (from hexane–benzene); *m*/*z* 316 (M^+, 15%) and 204 (100); M, 316.4; for UV data see Table 4; ν_{max}/cm^{-1} 2180 (C≡N), 2100 (C≡C), 1620 (C=N), 1600 (C=C) and 980 (*E*-HC=CH); for ^{1}H NMR data see Table 1; δ_C 185.2 (C-1: C=N), 147.0 (C-12: C–H^B), 146.2 (C-5 or -10), 145.2 (C-3), 145.0 (C-10 or -5), 135.0 (C-11: C–H^C), 134.7 (C-4), 128.7 (C-13: C–H^A), 124.4 (C-2), 114.2 (C≡N), 98.6 (C-7 or -8), 98.1 (C-

8 or -7), 90.0 (C-6 or -9), 89.5 (C-9 or -6), 35.2 (CMe_3), 35.1 (CMe_3), 28.7 (CMe_3), and 28.7 (CMe_3) (Found: C, 83.3; H, 7.7; N, 8.6. $C_{22}H_{24}N_2$ requires C, 83.5; H, 7.6; N, 8.85%).

N-*Cyano*-7,12-*dimethylcyclopentadeca*-2,4,6,12,14-*pentaene*-8,10-*diynylidenamine* **10**.—To a stirred solution of dimethyltetradehydro[15]annulenone **7**[2b] (407 mg, 1.73 mmol) in dry benzene (45 cm^3) was added dropwise a solution of titanium tetrachloride (0.90 cm^3, 8.65 mmol) in dry benzene (16 cm^3) during 1 h. Then a solution of compound **4** (1.60 g, 8.65 mmol) in dry benzene (12 cm^3) was added dropwise during 1 h. After being stirred for 37 h the mixture was worked up as for the isolation of compound **8**. The product was chromatographed on silica gel (3.3 × 7.2 cm). The fractions eluted with hexane–benzene (1:4) afforded the *tetradehydro*[15]*annulene* **10** (119 mg, 27%). It formed red needles, m.p. 208–210 °C (decomp.) (from hexane–benzene); *m/z* 258 (M^+, 17%) and 202 (100); M, 258.3; for UV data see Table 4; ν_{max}/cm^{-1} 2160 (C≡N), 2100 (C≡C), 1605 (C=N), 1595 (C=C) and 980 (*E*-HC=CH) (Found: C, 83.6; H, 5.6; N, 10.7. $C_{18}H_{14}N_2$ requires C, 83.7; H, 5.5; N, 10.8%). The ^1H NMR data showed that compound **10** consisted of two isomers, in the ratio 7:3 see Tables 1 and 3 and Figs. 2 and 3. The major isomer **10a**: δ_C 180.5 (C-1: C=N), 142.0 (C-14: C–H^B), 141.1 (C-6), 139.3 (C-3), 138.6 (C-13: C–H^C), 135.2 (C-5), 128.7 (C-4), 127.5 (C-15: C–H^A), 125.4 (C-7 or -12), 124.1 (C-2), 121.7 (C-12 or -7), 115.8 (C≡N), 92.4 (C-9 or -10), 89.3 (C-10 or -9), 86.6 (C-8 or -11), 84.8 (C-11 or -8), 22.1 (12-Me) and 21.0 (7-Me); the minor isomer **10b**: δ_C 179.8 (C-1: C=N), 142.9 (C-14), 141.6 (C-3), 141.0 (C-6), 139.4 (C-13: C–H^C), 134.9 (C-2), 133.2 (C-5), 133.0 (C-15: C–H^A), 128.7 (C-4), 126.8 (C-7 or -12), 125.6 (C-12 or -7), 116.0 (C≡N), 92.4, (C-9 or -10), 89.6 (C-10 or -9), 85.9 (C-8 or -11), 84.9 (C-11 or -8), 21.9 (12-Me) and 20.9 (7-Me).

N-*Cyano*-7,12-*dimethylcycloheptadeca*-2,4,6,12,14,16-*hexaene*-8,10-*diynylidenamine* **13**.—To a stirred solution of dimethyltetradehydro[17]annulenone **11**[2b] (350 mg, 1.35 mmol) in dry benzene (47 cm^3) was added dropwise a solution of titanium tetrachloride (0.57 cm^3, 5.40 mmol) in dry benzene (21 cm^3) during 1 h. Then a solution of compound **4** (1.00 g, 5.40 mmol) in dry benzene (10 cm^3) was added dropwise during 1.5 h. After being stirred for 2 days the mixture was worked up as for the isolation of compound **8**. The product was chromatographed on silica gel (3.2 × 7.5 cm). The fractions eluted with hexane–dichloromethane (2:3) afforded the *tetradehydro*[17]*annulene* **13** (172 mg, 45%). It formed brown needles, m.p. 218–219 °C (decomp.) (from hexane–benzene); *m/z* 284 (M^+, 36% and 228 (100); M, 284.3; ν_{max}/cm^{-1} 2170 (C≡N), 2120 (C≡C), 1610 (C=N), 1600 (C=C) and 995 (*E*-HC=CH); for UV data see Table 4; for ^1H NMR data see Tables 1 and 3 and Fig. 2; δ_C 186.3 (C-1: C=N), 153.5 (C-16: C–H^B), 151.8 (C-3), 143.6 (C-5), 143.1 (C-14: C–H^D), 139.2 (C-13: C–H^E), 139.1 (C-6), 128.5 (C-15: C–H^C), 128.0 (C-4), 126.2 (C-12), 126.2 (C-7), 124.7 (C-17: C–H^A), 121.2 (C-2), 115.0 (C≡N), 87.9 (C-9), 87.9 (C-10), 84.0 (C-8 or -11), 83.9 (C-11 or -8), 20.7 (7-Me) and 20.7 (12-Me) (Found: C, 84.8; H, 5.8; N, 9.7. $C_{20}H_{16}N_2$ requires C, 84.5; H, 5.7; N, 9.85%).

N-*Cyano*-9,14-*dimethylcyclononadeca*-2,4,6,8,14,16,18-*heptaene*-10,12-*diynylidenamine* **14**.—To a stirred solution of dimethyltetradehydro[19]annulenone **12**[2b] (69 mg, 0.24 mmol) in dry benzene (27 cm^3) was added dropwise a solution of titanium tetrachloride (0.026 cm^3, 0.24 mmol) in dry benzene (1 cm^3) during 30 min. Then a solution of compound **4** (94 mg, 0.48 mmol) in dry benzene (0.84 cm^3) was added dropwise during 45 min. After being stirred for 41 h the mixture was worked up as for the isolation of compound **8**. The product was chromatographed on silica gel (3.2 × 5.5 cm). The fractions eluted with benzene afforded the *tetradehydro*[19]*annulene* **14** (30 mg, 41%). It formed dark brown needles, m.p. 222–223 °C (decomp.) (from hexane–benzene); *m/z* 310 (M^+, 8%) and 149 (100) (chemical ionization method); M, 310.3; for UV data see Table 4; ν_{max}/cm^{-1} 2250 (C≡N), 2180 (C≡N), 2130 (C≡C), 1630 (C=N), 1600 (C=C) and 1000 and 980 (*E*-HC=CH); for ^1H NMR data see Tables 1 and 3 and Fig. 2; δ_C 182.7 (C-1: C=N), 138.5 (C-6), 138.4 (C-5), 138.1 (C-3), 136.2 (C-18: C–H^B), 134.8 (C-19: C–H^A), 132.8 (C-7), 132.7 (C-8), 131.7 (C-16: C–H^D), 130.2 (C-9 or -14), 128.6 (C-17: C–H^C), 127.4 (C-4), 126.4 (C-14 or -9), 126.0 (C-15), 120.5 (C-2), 118.8 (C≡N), 85.9 (C-11 or -12), 85.6 (C-12 or -11), 84.8 (C-10 or -13), 82.3 (C-13 or -10), 26.6 (9-Me) and 22.3 (14-Me) (Found: C, 87.4; H, 4.75; N, 9.05. $C_{22}H_{18}N_2$ requires C, 85.1; H, 5.85; N, 9.0%). Attempts to improve the elemental analysis failed.

N-*Cyano*-11-*methyl*-12,13,14,15-*tetradehydro*-7H-*benzocyclotrideca*-7-*ylidenamine* **17**.—To a stirred solution of monobenz[13]annulenone **15**[13] (170 mg, 0.697 mmol) in dry benzene (18 cm^3) was added dropwise a solution of titanium tetrachloride (0.39 cm^3, 3.7 mmol) in dry benzene (6 cm^3) during 30 min. Then a solution of compound **4** (0.68 g, 3.7 mmol) in dry benzene (6 cm^3) was added during 1.5 h. After being stirred for 26 h the mixture was worked up as for the isolation of compound **8**. The product was chromatographed on silica gel (3.2 × 9.0 cm). The fractions eluted with hexane–benzene (1:4) afforded the *monobenz*[13]*annulene* **17** (112 mg, 60%). It formed red needles, m.p. 179–179 °C (decomp.) (from hexane–benzene); *m/z* 268 (M^+, 100%); M, 268.3; for UV data see Table 4; ν_{max}/cm^{-1} 2265 (C≡N), 2100 (C≡C), 1620 (C=N), 1590 (C=C) and 980 (*E*-HC=CH) (Found: C, 85.3; H, 4.6; N, 10.1. $C_{19}H_{14}N_2$ requires C, 85.05; H, 4.5; N, 10.4%). The ^1H NMR spectrum indicates that compound **17** comprises two isomers in the ratio 5:4, see Tables 1 and 3 and Fig. 1. The major isomer **17a**: δ_C 185.7 (C-7: C=N), 147.0 (C-9: C–H^B), 143.1 (C-5), 142.2 (C-b), 140.1 (C-10: C–H^C), 130.7 (C-3), 130.4 (C-11), 130.1 (C-2), 129.1 (C-8: C–H^A), 128.6 (C-1), 127.9 (C-4), 124.6 (C-6), 122.2 (C-a), 114.3 (C≡N), 98.2 (C-13 or -14), 97.0 (C-14 or -13), 88.5 (C-12 or -15), 83.4 (C-15 or -12) and 20.2 (11-Me); the minor isomer **17b**: δ_C 185.4 (C-7: C=N), 145.5 (C-9: C–H^B), 144.3 (C-5), 142.0 (C-b), 139.7 (C-10: C–H^C), 132.2 (C-11), 130.6 (C-3), 129.9 (C-2), 129.1 (C-1), 127.8 (C-6), 127.7 (C-4), 124.6 (C-8: C–H^A), 121.7 (C-a), 114.1 (C≡N), 97.6 (C-13 or -14), 97.5 (C-14 or -13), 89.3 (C-12 or -15), 82.6 (C-15 or -12) and 20.2 (11-Me).

N-*Cyano*-14,15,16,17-*tetradehydro*-7H-*dibenzo*[a,g]*cyclotridecen*-7-*ylidenamine* **18**.*—To a stirred solution of dibenz[13]annulenone **16**[13] (200 mg, 0.714 mmol) in dry benzene (120 cm^3) was added dropwise a solution of titanium tetrachloride (0.20 cm^3, 1.79 mmol) in dry benzene (5.5 cm^3) during 1 h. Then a solution of compound **4** (0.35 g, 1.79 mmol) in dry benzene (4 cm^3) was added dropwise during 30 min. After being stirred for 3 days the mixture was worked up as for the isolation of compound **8**. The product was chromatographed on silica gel (3.2 × 12.0 cm). The fractions eluted with hexane–benzene (3:7) afforded the *dibenz*[13]*annulene* **18** (83 mg, 38%). It formed orange cubes, m.p. 146–147 °C (decomp.) (from hexane–benzene); *m/z* 304 (M^+, 100%); M, 304.3; for UV data see Table 4; ν_{max}/cm^{-1} 2180 (C≡N), 1630 and 1620 (C=N), 1600 (C=C) and 985 (*E*-HC=CH); for ^1H NMR data see Tables 1 and 3 and Fig. 1; δ_C 185.7 (C-7: C=N), 145.1 (C-5), 144.1 (C-9: C–H^B), 141.1 (C-b or -c), 141.0 (C-c or -b), 130.6 (C-2), 130.4 (C-12), 130.3 (C-3), 130.2 (C-11), 129.0 (C-13), 128.3 (C-1), 128.0 (C-10), 127.7 (C-6), 127.7 (C-4), 124.4 (C-8: C–H^A), 122.8 (C-d or -a), 122.1 (C-a or -d), 114.2 (C≡N), 94.9 (C-15 or -16), 94.5

* *Systematic name:* *N*-cyano-5,6,7,8-tetradehydro-15*H*-dibenzo[*a*,*g*]-cyclotridecen-15-ylidenamine.

(C-16 or -15), 85.0 (C-14 or -17) and 83.6 (C-17 or -14) (Found: C, 86.9; H, 4.3; N, 9.6. $C_{22}H_{12}N_2$ requires C, 86.8, H, 4.0; N, 9.2%).

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References

1 T. Asao, N. Morita, J. Ojima and M. Fujiyoshi, *Tetrahedron Lett.*, 1978, 2795; N. Morita, T. Asao, J. Ojima and K. Wada, *Chem. Lett.*, 1981, 57; N. Morita, T. Asao, J. Ojima and S. Hamai, *Chem. Lett.*, 1983, 1887; T. Asao, N. Morita, J. Ojima, M. Fujiyoshi, K. Wada and S. Hamai, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1713; J. Ojima, K. Itagawa and T. Nakada, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1723.

2 (*a*) T. M. Cresp, J. Ojima and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 2130; (*b*) J. Ojima, Y. Shiroishi, K. Wada and F. Sondheimer, *J. Org. Chem.*, 1980, **45**, 3564.

3 S. Kuroda, K. Kitatani and J. Ojima, *Tetrahedron Lett.*, 1982, **23**, 2657; S. Kuroda, J. Ojima, K. Kitatani, M. Kirita and T. Nakada, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2987.

4 J. Ojima, K. Itagawa, S. Hamai, T. Nakada and S. Kuroda, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2997.

5 J. Ojima, S. Ishizaka, Y. Shiraiwa, E. Ejiri, T. Kato, S. Kuroda and H. Takeda, (*a*) *Chem. Lett.*, 1986, 1295; (*b*) *J. Chem. Soc., Perkin Trans. 1*, 1987, 1505.

6 T. Wada, J. Ojima, A. Yamada, A. F. Garito and H. Sasabe, *SPIE Proc.*, 1989, **1147**, 286; J. Ojima, K. Kitamura, H. Sugimori, H. Higuchi and M. Iyoda, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3238.

7 Part of this work has appeared in preliminary form; J. Ojima, H. Higuchi, Y. Sata, H. Yamamoto, T. Koizumi, M. Iyoda and G. Yamamoto, *Chem. Lett.*, 1991, 507.

8 For reviews, see E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41; F. Pietra, *Chem. Rev.*, 1973, **73**, 203; G. Becker in *Houben-Weyl, Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1985, vol. V, IIc, pp. 697–709.

9 S. Iwatsuki, T. Itoh and H. Itoh, *Chem. Lett.*, 1988, 1187.

10 M. R. Bryce and S. R. Davies, *J. Chem. Soc., Chem. Commun.*, 1989, 328.

11 L. Birkofer, A. Ritter and P. Richter, *Tetrahedron Lett.*, 1962, 195.

12 M. Iyoda, S. Tanaka, K. Nishioka and M. Oda, *Tetrahedron Lett.*, 1983, **24**, 2861.

13 J. Ojima and M. Fujiyoshi, *J. Chem. Soc., Perkin Trans. 1*, 1980, 466.

14 L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, London, 1969, pp. 280–304.

15 J. Ojima, M. Masumoto, J. Katsuyama, K. Kitamura and M. Iyoda, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1188.

16 M. Iyoda and M. Nakagawa, *Chem. Lett.*, 1975, 815.

17 J. Ojima, E. Ejiri, T. Kato, M. Nakamura, S. Kuroda, S. Hirooka and M. Shibutani, *J. Chem. Soc., Perkin Trans. 1*, 1987, 831.

18 J. Ojima, S. Kuroda and M. Kirita, *Chem. Lett.*, 1982, 1371.

19 M. Nakagawa, *Pure Appl. Chem.*, 1975, **44**, 885; B. A. Hess, Jr., L. S. Schaad and M. Nakagawa, *J. Org. Chem.*, 1977, **42**, 1669.

20 H.-O. Kalinowski and H. Kessler, *Top. Stereochem.*, 1973, **7**, 295; L. M. Jackman in *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Academic, London, 1975, pp. 203–252.

21 N. Darby, T. M. Cresp and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 1960.

22 See P. J. Garratt and K. Grohmann, in *Houben-Weyl, Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1972, vol. V, Id, pp. 533–535.

23 D. A. Kleier and G. Binsch, *QCPE*, No. 165.

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