'ACETYLENE–CUMULENE' DEHYDROANNULENES

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ABSTRACT

The synthesis of tetrasubstituted tetradehydro[18]- and [22]annulenes containing a diacetylene and a hexapentaene unit has been accomplished by reductive dehydroxylation of corresponding 18-membered and 22-membered cyclic glycols. On the basis of these studies, a general method of preparation of tetrasubstituted didehydro[4n + 2]annulenes containing an acetylene and a butatriene unit has been developed. The didehydro[4n + 2]annulenes (n = 3 ~ 7) were found to be diatropic and to have high conformational stability. The n.m.r. spectral properties of the didehydroannulenes have been discussed. The synthesis of didehydro[14]annulenes annelated with naphthalene or benzene has been achieved, and the effect of annelation on π-electron delocalization of the annulene ring has been discussed.

INTRODUCTION

1,8-Didehydro[14]annulene (1) obtained by Sondheimer[1–4] holds a unique position in a wide variety of dehydroannulenes, i.e. it contains formal acetylenic and cumulenic linkages in the cyclic system and classical equivalent Kekulé structures (1a and 1b) can be written in contrast to

| 1a | 1b | 2 |

F. Sondheimer

ordinary dehydroannulenes containing only acetylenic bond(s) in which no equivalent resonance structures can be drawn. 1,8-Didehydro[14]-annulene (1) is better represented by a symmetrical formula (2). We have been interested in the synthesis and properties of this type of symmetrical 'acetylene–cumulene' dehydroannulenes and developed general methods of synthesis of tetradehydro[4n + 2]annulenes (n = 4 and 5) and didehydro-[4n + 2]annulenes (n = 3 ~ 7). The series of diatropic 'acetylene–cumulene' dehydroannulenes which is the subject of the present paper is a tiny twig of a big tree grown on the ground of pioneering theoretical works by Professor Hückel[5] and of magnificent experimental works by Professor Sondheimer[6].
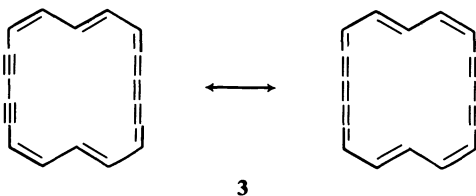
TETRADEHYDRO[4n + 2]ANNULENES

Our first efforts were directed to the synthesis of tetradehydro[18]-annulene (3) having a diacetylene and a hexapentaene unit in the conjugated system. *cis*-Isomer of 3-substituted-2-penten-4-ynal (5) predominantly

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formed by anionotropic rearrangement of β-chlorovinylethynylcarbinol (4) by acid treatment was used as starting material[7]. The aldol condensation of the aldehyde (5) with methyl ketone afforded diene ketone (6) which was oxidatively coupled by means of cupric acetate in pyridine to give diketone (7). Bis-ethynylation of the diketone (7) to yield bis-ethynyl diol (8) could be
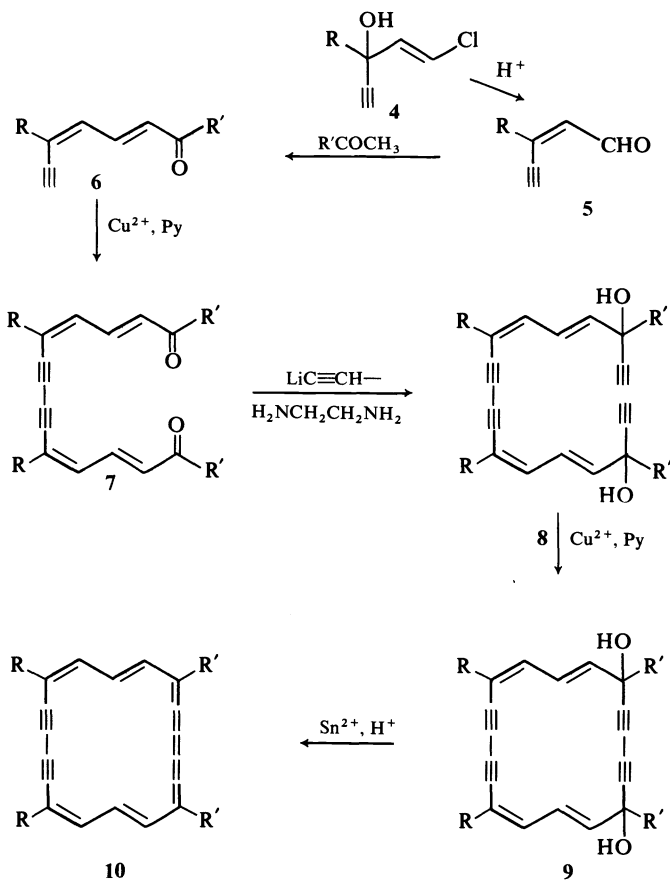
achieved by lithium acetylide–ethylenediamine complex[8] in organic solvent. Oxidative coupling of the bis-ethynyl diol (8) by cupric acetate in pyridine under a high dilution condition using ether as an entraining solvent resulted in the formation of 18-membered cyclic glycol (9) in a rather high yield. Usually the cyclic glycol (9) could be separated into meso and racemic diastereomers. Treatment of the cyclic glycol (9) with stannous chloride dihydrate in hydrochloric acid or in ether saturated with hydrogen chloride yielded highly coloured tetrasubstituted tetradehydro[18]annulene (10) in a high yield. According to this reaction sequence, we have prepared tetra-dehydro[18]annulenes bearing various substituent groups, shown in *Table 1*. All of these tetradehydro[18]annulenes (10a–f) gave 1:1 CT-complex with 2,4,7-trinitrofluorenone. As shown in *Table 1*, induction of strong diamagnetic ring current in the tetradehydro[18]annulenes (10a–f) was revealed by their n.m.r. spectra.

Tetramethyl- and dimethyl-diphenyl derivatives (10a and 10b) showed almost temperature independent n.m.r. spectra indicating high conformational stability of the tetradehydro[18]annulene skeleton. Introduction of phenyl groups caused appreciable stabilization of the tetradehydro[18]-annulene. However, regular bathochromic shift of the electronic spectra along with the increase of phenyl substitution reveals that the phenyl group exerts prominent perturbation on the tetradehydroannulene system. Moreover, the fact that the phenyl substituted annulenes are sparingly soluble in n.m.r. solvents brought about experimental difficulty. Consequently, it was considered to be important to discover a substituent group which exerts minor perturbation on the annulene ring and increase both stability and solubility in n.m.r. solvents. We have chosen the *t*-butyl group as the most promising candidate. Tetra-*t*-butyl derivative (10f) was found to be much more stable and much more soluble in n.m.r. solvents than the other analogues. The electronic spectrum of the tetra-*t*-butyl derivative (10f) was almost superimposable with that of tetramethyl analogue (10a) indicating minor electronic perturbation of *t*-butyl groups on the annulene nucleus. Also the yields and crystallinity of the *t*-butyl derivative including various intermediates were found superior to those of the other derivatives. This is the reason why we have mainly used *t*-butyl group as substituent in the following studies.

The n.m.r. spectra of these tetradehydro[18]annulenes (10a–f) indicate that the formal diacetylene and hexapentaene units incorporated in the aromatic annulene rings should be identical just as the formal double and single bonds in the Kekulé structure of benzene. With the purpose of proving the identity of acetylenic and cumulenic linkages by chemical means, we have prepared isomeric bis-ethynyl diols (11a and 11b) which were converted into isomeric cyclic glycols (12 and 13). Dehydroxylative aromatization of the cyclic glycols (12 and 13) yielded di-*t*-butyl-diphenyltetradehydro[18]-annulenes (14 and 15). The tetradehydro[18]annulenes (14 and 15), thus prepared, were found to be identical in every respect. They showed the same decomposition points (189.0–191.0°C) and gave superimposable i.r. spectra. Their electronic spectral data are summarized in *Table 2*. The wavelengths of absorption maxima were found to be identical in both tetradehydro[18]-annulenes (14 and 15), and the absorption intensities also agreed within the

Table 1. N.m.r. spectra of tetradehydro[18]annulenes

τ values

	R	R'	H^a	H^b	H^c	Me	t–Bu	Ref.
a	Me	Me		0.34	15.24	7.42		9
b	Me	Ph	0.12	0.54	14.20	6.56		10
c	Ph	Ph	−0.31		13.19			11
d	p-MeO-Ph	p-MeO-Ph	−0.04		13.00			12
e	t–Bu	Ph	−0.40	−0.01	13.90		7.93	13
f	t–Bu	t–Bu	0.02		14.92		7.89	10
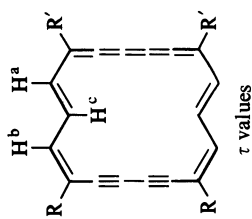
HO
Ph ⟋⟍ Bu^t
Ph Bu^t
HO
12

Ph ⟋⟍ Bu^t
Ph Bu^t
14

R R'
HO
R R'
11 HO

a:R = Ph, R' = Bu^t
b:R = Bu^t, R' = Ph

HO
Bu^t Ph
Bu^t Ph
HO
13

Bu^t Ph
Bu^t Ph
15

Table 2. Electronic spectra. λ_{max} in nm ($\varepsilon \times 10^{-2}$) in THF
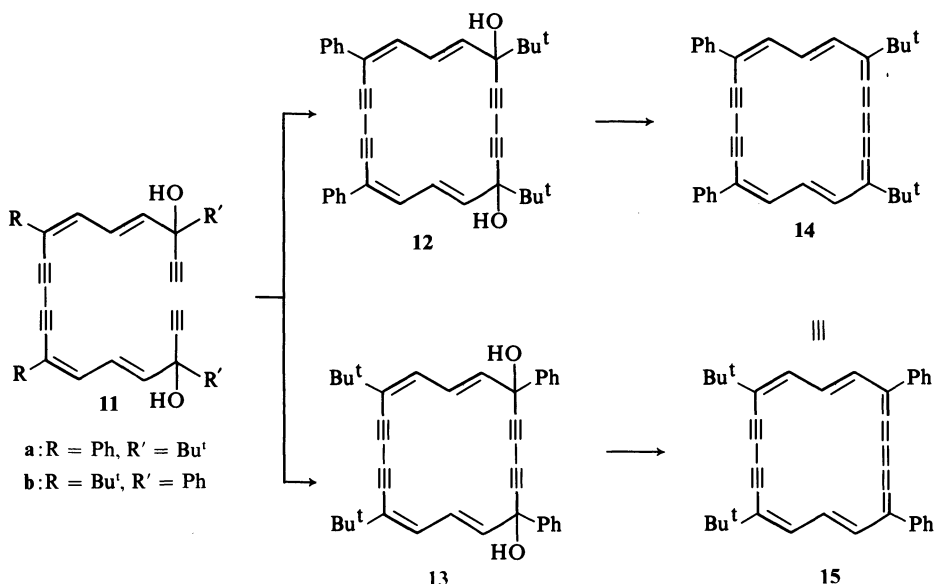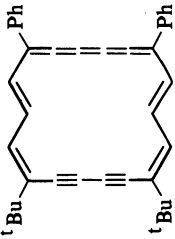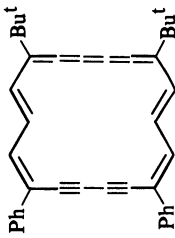
Structure	Data
^{t}Bu ... Ph / ^{t}Bu ... Ph	231*(288) 245*(160) 256.5(179) 270*(153) 277.5(176) 299(142) 325*(152) 347*(303) 368*(373) 386*(616) 402 (2200) 544*(164) 587(875) 670*(4.80) 740(21.7)
Ph ... ^{t}Bu / Ph ... ^{t}Bu	231*(285) 245*(162)256.5(177) 270*(152) 277.7(175) 299(142) 325*(151) 347*(303) 368*(374) 386*(614)402(2190) 544*(164) 587(873) 670*(4.72) 740(21.6)

* Shoulder.

experimental error being about one per cent in the short wavelength region. As shown in *Table 3*, the n.m.r. spectra of both dehydroannulenes (**14** and **15**) were also found to be identical within the experimental error being the difference of chemical shifts within $\tau \pm 0.02$. These results can be regarded as chemical evidence for the identity of diacetylene and hexapentaene units incorporated in the aromatic annulene system[13].

Argon Laser Raman spectra of the tetradehydro[18]annulenes (**14** and **15**) are shown in *Figure 1*. The annulenes (**14** and **15**) exhibit single absorption due to stretching vibration of *sp—sp* carbon linkage at 2080 cm^{-1}. This is further physical evidence for the identity of acetylenic and cumulenic linkages in addition to the n.m.r. spectral one.

Table 3. 60 MHz n.m.r. spectra in THF-d_8

Protons	Compounds					
	^{t}Bu / Ph structure			^{t}Bu / Ph (Bu^{t}) structure		
Outer protons adjacent to phenyl	−0.40	d(14 Hz)	1H	−0.40	d(14 Hz)	1H
Outer protons adjacent to t-butyl	−0.01	d(14 Hz)	1H	0.01	d(14 Hz)	1H
o-Protons of phenyl	1.13	m	2H	1.15	m	2H
m, p-Protons of phenyl	2.37	m	3H	2.39	m	3H
Protons of t-butyl	7.93	s	9H	7.93	s	9H
Inner protons	13.90	t(14 Hz)	1H	13.90	t(14 Hz)	1H

Internal standard: TMS.

Figure 1. Laser Raman spectra of di-*t*-butyl-diphenyltetrahydro[18]annulenes.

In view of the strong diamagnetic ring current and high conformational stability of the tetradehydro[18]annulenes (10a–f), it was considered to be of interest to synthesize a 22π-electron system having an analogous rigid molecular framework. The condensation reaction of ethyl vinyl ether with acetal proposed by Isler[14] was used for the extension of the ethylenic bond. The reaction of diethyl acetal (16) with ethyl vinyl ether in the presence of boron trifluoride afforded ethoxy acetal (17) which was treated with acid to give dienealdehyde (18). The aldol condensation of the aldehyde (18) with methyl ketone gave triene ketone (19). Oxidative coupling of the triene ketone (19) by cupric acetate in pyridine followed by ethynylation of the resulting diketone (20) with lithium acetylide–ethylenediamine complex[8] yielded bis-ethynyl alcohol (21). Intramolecular cyclization of the bis-ethynyl alcohol (21) under a high dilution condition by cupric acetate in pyridine afforded 22-membered cyclic glycol (22) in a fairly high yield. Tetrasubstituted tetradehydro[22]annulene (23) was obtained as deeply coloured crystals by dehydroxylative aromatization of the cyclic glycol (22).

The 60 MHz n.m.r. spectrum of tetra-*t*-butyltetradehydro[22]annulene (23, R = *t*-Bu) measured at 30°C is shown in *Figure 2*. The spectrum indicates that the [22]annulene (23, R = *t*-Bu) sustains a strong diamagnetic ring current holding the molecular configuration shown in *Figure 2*. The spectrum measured at − 40°C shows no essential change indicating high conformational stability of this molecule. Tetraphenyltetradehydro[22]annulene (23, R = Ph) was found to be sparingly soluble in n.m.r. solvents. However, the FT–n.m.r. spectrum revealed that the tetradehydro[22]annulene (23, R = Ph) is strongly diatropic as shown in *Table 4*.
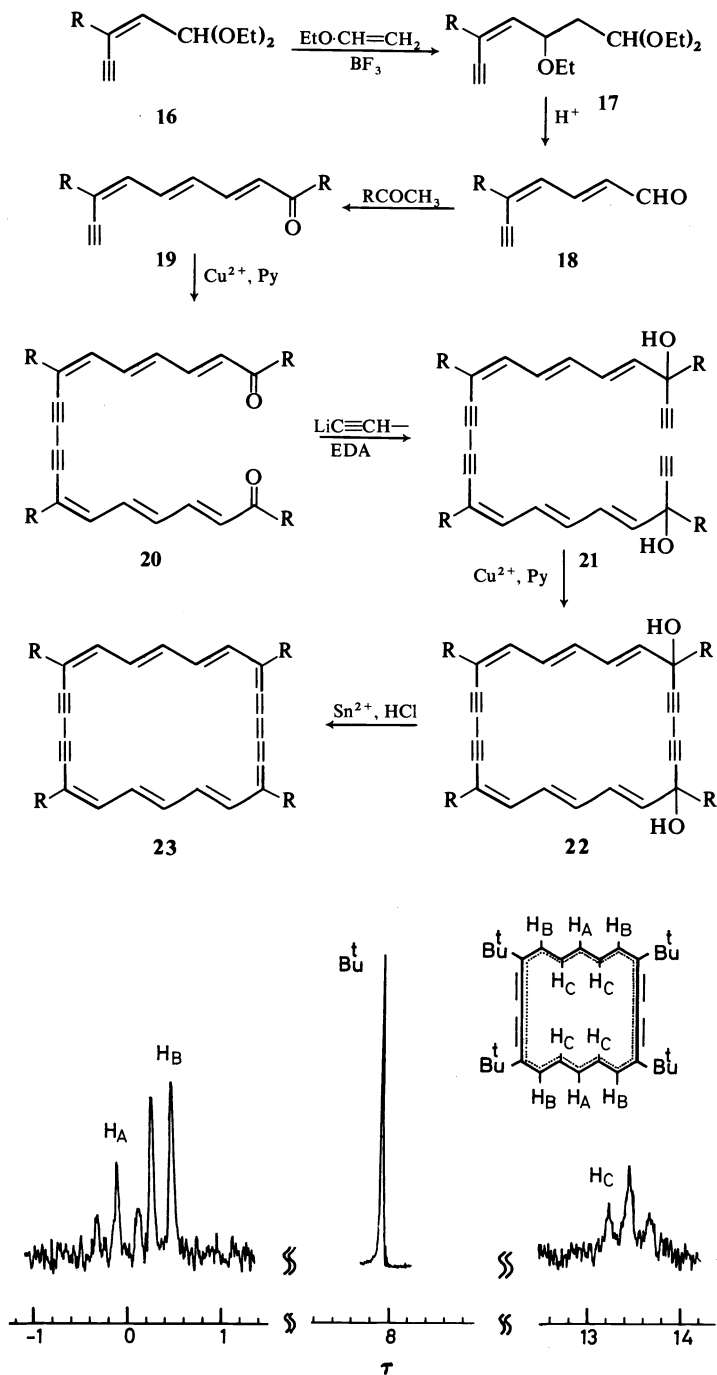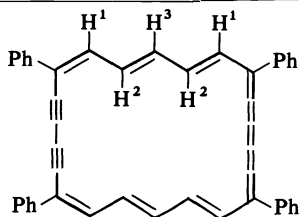
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Figure 2. 60 MHz n.m.r. spectrum of tetra-*t*-butyltetradehydro[22]annulene in CDCl₃ at 30°C.

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Table 4. 100 MHz FT–n.m.r. spectrum of tetraphenyltetradehydro[22]annulene in THF–d_8 at $-40°C$

H^1	-0.72	d	$J = 14$ Hz
H^3	-0.79	t	$J = 14$ Hz
H^2	12.80	t	$J = 14$ Hz

black violet
cryst.

DIDEHYDRO[4*n* + 2]ANNULENES

Now I would like to turn to the studies on didehydro[4*n* + 2]annulenes. As previously mentioned, 18-membered cyclic glycols (**9**) were obtained by oxidative coupling of bis-ethynyl alcohols (**8**) in unexpectedly high yields. The results are summarized in *Table 5*. In the case of tetra-*t*-butyl derivative,

Table 5. Yields of intramolecular cyclization
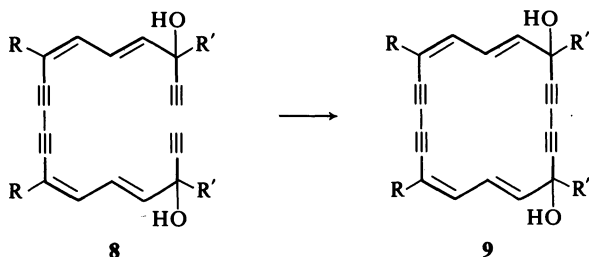
Substituents	Yields, %
R = R' = Me	69.3
R = Me, R' = Ph	67.0
R = R' = *t*-Bu	96.0
R = Ph, R' = *t*-Bu	71.0
R = *t*-Bu, R' = Ph	85.0

an almost quantitative yield has been attained. These results seem to be attributable to the configuration of bis-ethynyl alcohols (**8**) which is favourable to intramolecular cyclization, and seem to suggest the possibility of cyclic dimerization of ethynyldiene ketones (**6**) under appropriate reaction conditions. After several unsuccessful trials we have found that the cyclic dimerization can be realized on addition of diene ketone (**6**) in tetrahydrofuran to a suspension of finely powdered potassium hydroxide in liquid ammonia[15]. Treatment of the resulting glycol (**24**) with stannous chloride and hydrochloric acid yielded tetrasubstituted didehydro[14]annulene

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a : R = R′ = Bu-*t*
b : R = Ph, R′ = Bu-*t*
c : R = R′ = Ph

24
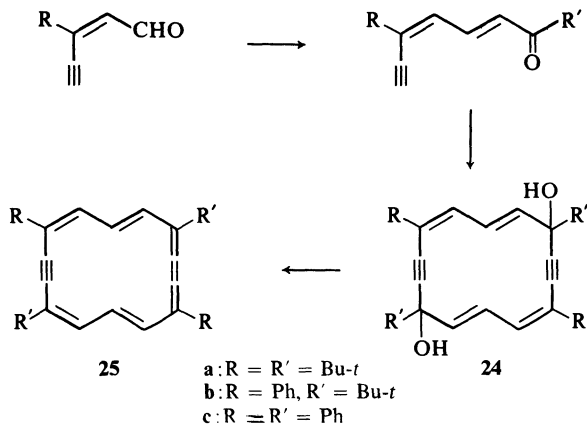
(25). As shown in *Table 6*, the didehydro[14]annulenes (25a–c) thus prepared were found to be strongly diatropic. It is interesting that the tetraphenyl derivative (25c) gave a CT-complex with two moles of trinitrofluorenone.

Table 6. Properties of tetrasubstituted didehydro[14]annulenes
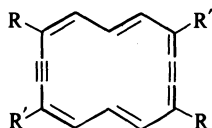
a : R = R′ = *t*-Bu
b : R = Ph, R′ = *t*-Bu
c : R = R′ = Ph

	Colour of cryst.	Outer-H	Inner-H	CT-complex
a	dark red	0.58	14.39	1 : 1
b	brown violet	0.12	13.42	1 : 1
c	violet	0.06	12.56	1 : 2

N.m.r. 60 MHz in THF-d$_8$.
CT-complex. annulene : trinitrofluorenone.

Because, at least at present, 1,8-didehydro[14]annulene is the parent compound of symmetrical 'acetylene–cumulene' dehydroannulenes, we have intended to reveal the fundamental nature of the symmetrical didehydroannulene nucleus using didehydro[14]annulene.
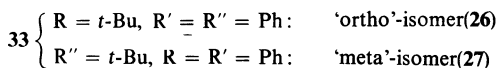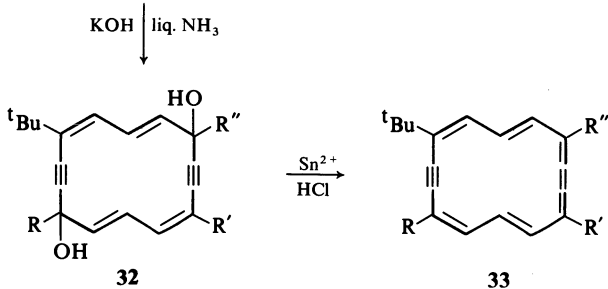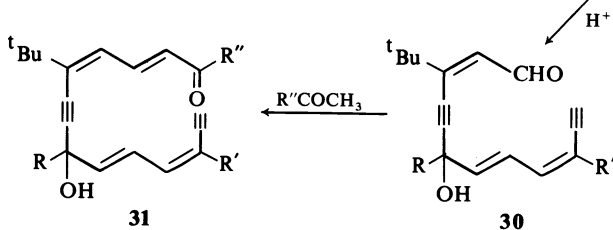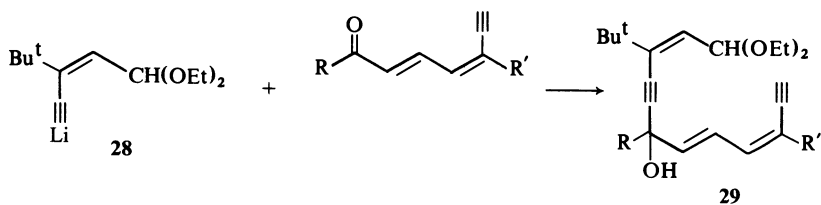
In the benzenoid series, it has been well-known that *o*-, *m*- and *p*-isomers exhibit interesting differences in their physical and chemical properties.

We have carried out the synthesis of position isomers of di-*t*-butyl-diphenyldidehydro[14]annulene which correspond to *o*-, *m*- and *p*-isomers of terphenyl[16]. Formal quinoid structures can be written in the cases of 'para'- and 'ortho'-isomers, but not in the case of the 'meta'-isomer just as the cases of *o*-, *p*- and *m*-terphenyls, respectively. The preparation of 'para'-isomers (25b) has already been discussed. The syntheses of 'ortho'- and 'meta'-isomers (26 and 27) were performed by stepwise reactions.

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'ortho'	'meta'	'para'
26	**27**	**25b**
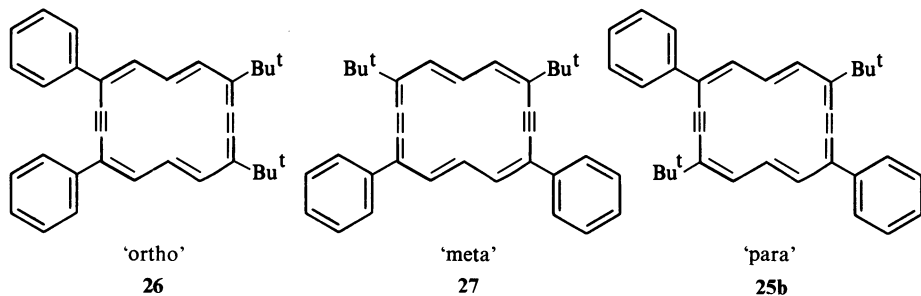
Diethyl acetal of *t*-butylpentenynal was converted into the lithio deriva-
tive (**28**) by an ethereal solution of phenyllithium. Reaction of diene ketone
with the lithio derivative (**28**) yielded hydroxy acetal (**29**) which was hydro-

$$\begin{cases} R = t\text{-Bu, } R' = R'' = Ph: & \text{'ortho'-isomer(26)} \\ R'' = t\text{-Bu, } R = R' = Ph: & \text{'meta'-isomer(27)} \end{cases}$$
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lysed to give ethynylaldehyde (**30**). The aldol condensation of the aldehyde
(**30**) with methyl ketone afforded ethynyl ketone (**31**). The ethynyl ketone
(**31**) dissolved in tetrahydrofuran was treated with potassium hydroxide
in liquid ammonia to give cyclic glycol (**32**). 'Ortho'- and 'meta'-isomers of

Table 7. Properties of position isomers of di-t-butyldiphenyldidehydro[14]annulene

	'o'-	'm'-	'p'-
Crystals	deep green plates	reddish green needles	brown violet needles
M.pt, °C	248.0–249.0	200.8–202.0	>200

N.m.r. spectra, $CDCl_3$, $J = 13.5$ Hz, τ

	'o'-	'm'-		'p'-
Inner-H	13.51, t	13.45, t	13.65, t	13.54, t
t-Bu	8.10, s	8.07, s		8.06, s
Ph-H(m,p)	2.38, m	2.40, m		2.43, m
Ph-H(o)	1.37, m	1.41, m		1.42, m
Outer-H adjacent to t-Bu	0.58, d	0.64, d		0.56, d
Outer-H adjacent to Ph	0.26, d	0.17, d		0.26, d

Electronic spectra, nm(ε) in THF

	'o'-	'm'-	'p'-
I	624(1800)	624(1270)	623(1640)
II	504(37200)	499(37100)	508(52600)
III	361(215000)	368(187000)	357(195000)

di-*t*-butyl-diphenyldidehydro[14]annulene (**26** and **27**) could be obtained by dehydroxylative aromatization of the corresponding cyclic glycol (**32**). As summarized in *Table 7*, the position isomers (**26, 27** and **25b**) exhibit closely related n.m.r. spectra. Also, the position isomers (**26, 27** and **25b**) showed similar electronic spectra. This fact indicates that the electronic transitions of these molecules are under the control of the transition of didehydro[14]annulene system, and also the close similarity of electronic spectra seemed to be related with the direction of polarization of didehydro–[14]annulene ring. Therefore, we have carried out the synthesis of a dimethoxy derivative of '*para*'-isomer.

Condensation of ω-methoxyacetophenone with *t*-butylpentenynnal yielded methoxy ketone (**34**) as an unstable liquid. Treatment of the ketone (**34**) with potassium hydroxide in liquid ammonia afforded diastereomers of cyclic glycol (**35**) as colourless crystals. Dimethoxydidehydro[14]annulene (**36**) was obtained as deep green plates by dehydroxylative aromatization of
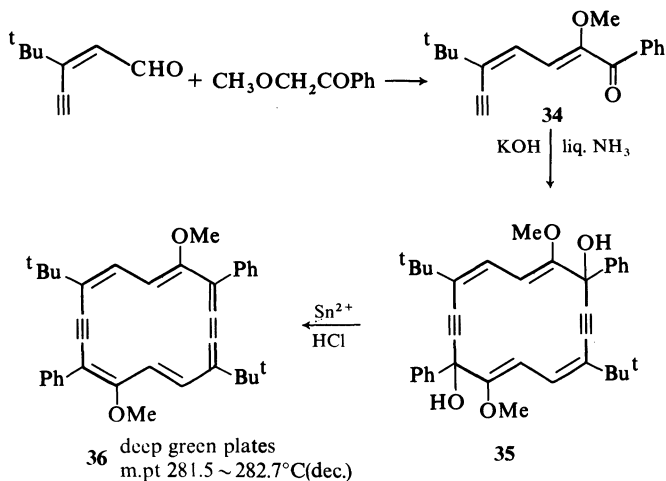
the cyclic glycol in 33 per cent yield based on the methoxy ketone (**34**). Electronic and n.m.r. spectral data of the dimethoxydidehydro[14]annulene (**36**) are shown in *Table 8*. The electronic spectra of '*ortho*'- (**26**), '*meta*'- (**27**),

Table 8. Electronic and n.m.r. spectra of di-*t*-butyldimethoxy-diphenyldidehydro[14]annulene

Electronic spectrum	N.m.r. spectrum, 100 MHz		
I : 637(4540)	Inner-H	13.76,	d
II : 492(35000)	*t*-Bu	8.15,	s
III : 356(177000)	OMe	6.09,	s
	Ph-H(*m, p*)	2.43,	m
	Ph-H(*o*)	1.51,	m
	Outer-H	0.49,	d

nm(ε) in THF. τ in CDCl$_3$.

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'*para*'- (**25b**) and dimethoxy derivatives (**36**) are illustrated in *Figure 3*. The dimethoxy derivative (**36**) gave a similar electronic spectrum to those of the other derivatives (**26, 27** and **25b**) except for intensification of the longest wavelength band (I). At first glance, this result seems to suggest that the direction of polarization of the longest wavelength band (I) is perpendicular to the axis which bisects the molecule through the midpoints of *sp—sp* carbon linkages.
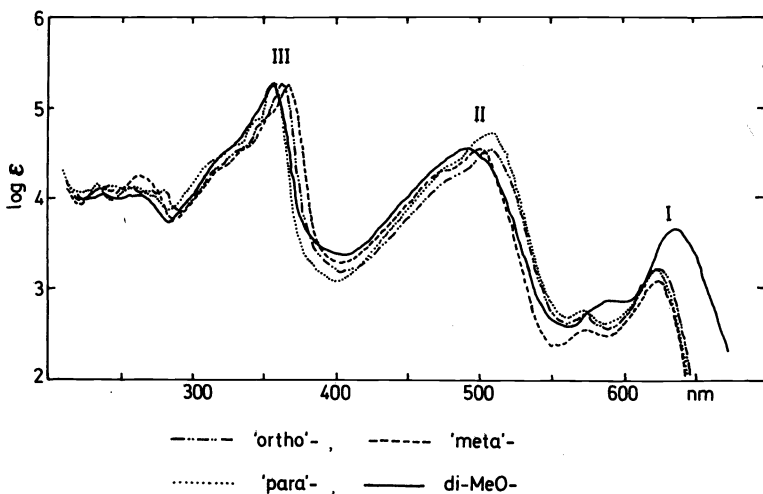

Figure 3. Electronic spectra of position isomers of di-*t*-butyl-diphenyldidehydro[14]annulene and dimethoxy derivative in THF.

However, quite recently, measurements of the fluorescence excitation spectra of tetra-*t*-butyldidehydro[14]annulene (**25a**) and '*para*'-isomer of di-*t*-butyl-diphenyldidehydro[14]annulene (**25b**), the polarized reflection spectrum of a single crystal of tetra-*t*-butyldidehydro[18]annulene (**38**) and the theoretical calculation by PPP and RPA methods on didehydro[14]- and [18]annulenes have been performed by Professor J. Tanaka in Nagoya University[17]. The nature of electronic transitions and the direction of polarization are firmly established on the basis of these investigations. Namely, as shown in *Figure 4*, the longest wavelength band (I) is ^1L_b species and the direction of polarization is parallel to the axis, the medium wavelength band (II) is ^1L_a species having perpendicular polarization and the short wavelength band (III) consists of parallel polarized ^1B_b species and perpendicular polarized ^1B_a species.

The fluorescence excitation spectrum of the '*para*'-isomer (**25b**) is shown in *Figure 5*. The arrows indicate the positions of the absorption maxima. The spectrum indicates clearly the direction of polarization of each electronic transition.

Further studies on the nature of didehydro[14]annulene nucleus are now in progress.
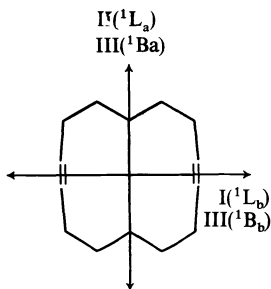
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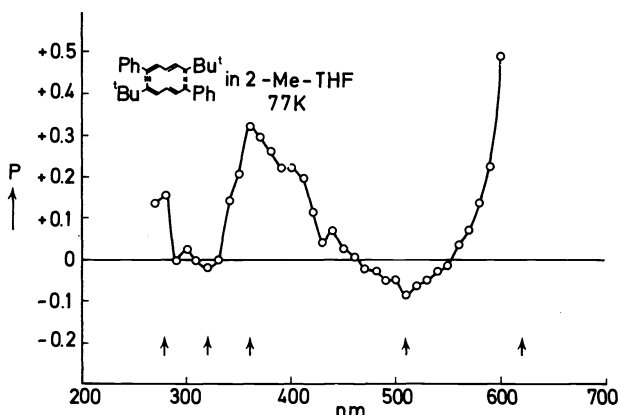Figure 4. Directions of polarization of didehydro[14]annulene.

Figure 5. Excitation fluorescence spectrum (APF) of di-*t*-butyl-diphenyldidehydro[14]annulene (25b). Measured by M. Morita in Nagoya University.
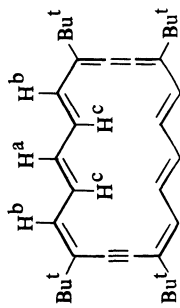
Now I would like to proceed to the synthesis of higher members of didehydro[$4n + 2$]annulenes. If the above-mentioned cyclic dimerization of ethynyldiene ketone can be realized for triene or tetraene ketone, it opens a new route for the synthesis of didehydro[18]- or [22]annulene.

In fact, the cyclic dimerization is realized at first for triene ketone. Triene ketone (**19**, R = *t*-Bu) obtained from dienaldehyde (**18**, R = *t*-Bu) gave diastereomers of 18-membered cyclic glycol (**37**) in 66 per cent total yield on treatment with potassium hydroxide in liquid ammonia. Dehydroxylative aromatization of the cyclic glycol (**37**) yielded tetra-*t*-butyldidehydro[18] annulene (**38**) as deep reddish violet crystals in a yield of 93 per cent[18]. The mass spectrum exhibits a molecular ion peak consistent with the molecular weight of the annulene (**38**).

As shown in *Figure 6*, the n.m.r. spectrum of the didehydro[18]annulene (**38**) clearly indicates that the annulene (**38**) is strongly diatropic. It is to be noted that the outer proton (H_A) situated at the centre of the molecule exhibits its signal at the lowest field. The n.m.r. spectra of the didehydro[18]-annulene (**38**) measured at elevated temperatures in deuteriobromoform are

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t Bu ... CHO CH₃COBuᵗ, NaOH → $\xrightarrow{EtOH}$

18 (71%)

t Bu ... (with O) m.pt 92.5 ~ 93.5°

19 (66%) | KOH, liq. NH₃

t Bu ... t Bu ... t Bu ... t Bu

$\xleftarrow[- 60°]{\underset{HCl/ether}{SnCl_2 \cdot 2H_2O}}$

HO, t Bu ... t Bu ... OH

(93%)

m.pt. ~ 260° (dec.)
Mass(m/e) 454(M⁺)

38

a : m.pt.230.5 ~ 231.5°
b : m.pt170 ~ 171°

37

Bᵘ H_B H_A H_B Bᵘ
H_C H_C
Bᵘ Bᵘ

H_A   H_B   ᵗBu   H_C

0   1   8   13   14
τ

Figure 6. 60 MHz n.m.r. spectrum of tetra-t-butyl-didehydro[18]annulene in CDCl₃ at 36°C.

summarized in *Table 9*. The fact that the spectra showed no essential change indicates the high conformational stability of the didehydro[18]annulene skeleton.

The preliminary result of x-ray analysis of tetra-t-butyldidehydro[18] annulene (**38**) being performed recently by Dr Kabuto in the laboratory of Professor Kitahara[20] is shown in *Figure 7*. This result is still a preliminary one, but the highly symmetrical structure of the annulene (**38**) provided by

Table 9. 60 MHz n.m.r. spectra of tetra-t-butyldidehydro[18]annulene in CDBr$_3$ (τ)

Temp, °C	H^a	H^b	t-Bu	H^c
36	0.18, t $J = 13$ Hz	0.68, d $J = 13$ Hz	8.09, s	13.64, t $J = 13$ Hz
70	0.30, t $J = 13$ Hz	0.78, d $J = 13$ Hz	8.10, s	13.46, t $J = 13$ Hz
110	0.44, t $J = 13$ Hz	0.81, d $J = 13$ Hz	8.10, s	13.28, t $J = 13$ Hz

X - Ray Analysis

$C_{34}H_{46}$

$a = 10.165 \,\text{Å}$
$b = 15.908$
$c = 9.914$
$\beta = 108.54°$

$P_{2_1}/n \, (Z = 2)$
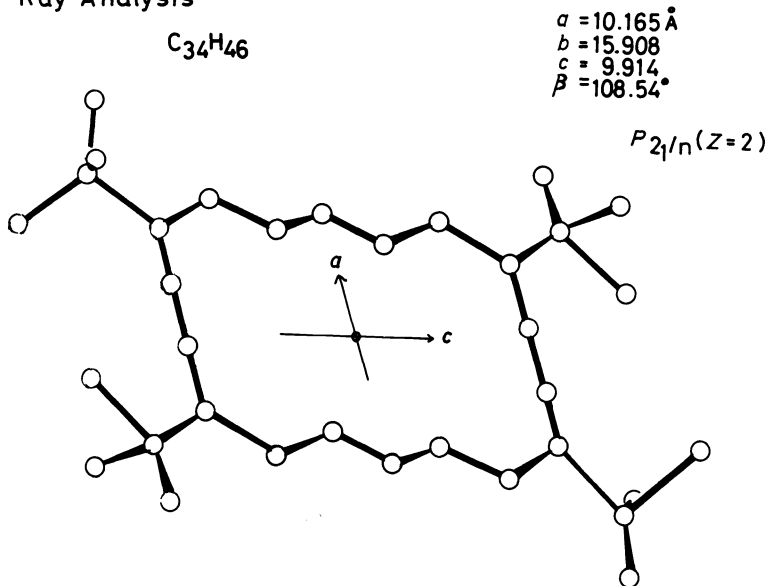
Figure 7. Molecular geometry of tetra-t-butyl-didehydro[18]annulene (38).

the x-ray analysis offers a further proof of aromaticity of the didehydro[18]-annulene system.

By a similar reaction sequence, we have prepared di-t-butyl-diphenyl- and tetraphenyl-didehydro[18]annulenes (39 and 40). The didehydro[18]-annulenes (39 and 40) were found to be diatropic as shown in Table 10. The tetraphenyl derivative (40) has extremely poor solubility in organic solvents and the measurement of its n.m.r. spectrum is barely accomplished by FT-technique. The electronic spectra of didehydro[18]annulenes (38, 39 and 40) are illustrated in Figure 8. The spectra were found to be closely related with those of the corresponding tetradehydro[18]annulenes (10f, 10e = 14 = 15 and 10c).

Thus, didehydro[18]annulenes were found to be strongly diatropic and much more stable than the corresponding tetradehydro[18]annulenes, and also proved to be conformationally stable. These satisfactory properties prompted us to the synthesis of didehydro[22]annulene[19].

A Grignard derivative of ethoxy acetal (41) was converted into a trimethyl-silyl derivative (42). Treatment of the trimethylsilyl derivative (42) with an aqueous acetic acid containing sodium acetate followed by re-acetalization afforded trimethylsilyl dienealdehyde diethyl acetal (43) in a high yield which gave ethoxy diene acetal (44) by the reaction with ethyl vinyl ether. The ethoxy diene acetal (44) was treated with an aqueous acetic acid and sodium acetate. The aldol condensation of the resulting trienealdehyde (45) with pinacolone gave tetraene ketone (46). 22-Membered cyclic glycol

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Table 10. N.m.r. spectra of di-*t*-butyl-diphenyl and tetraphenyldidehydro[18]annulenes (τ)
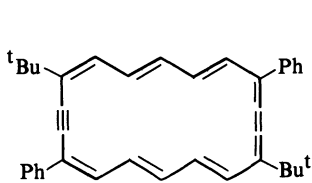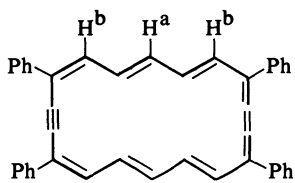
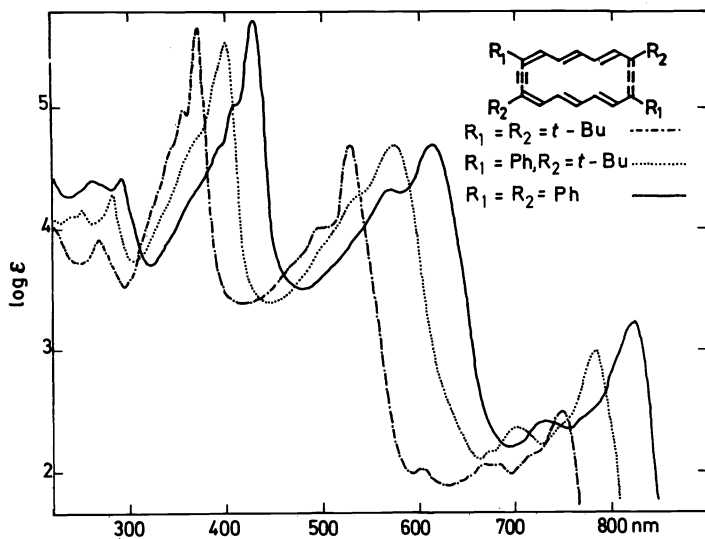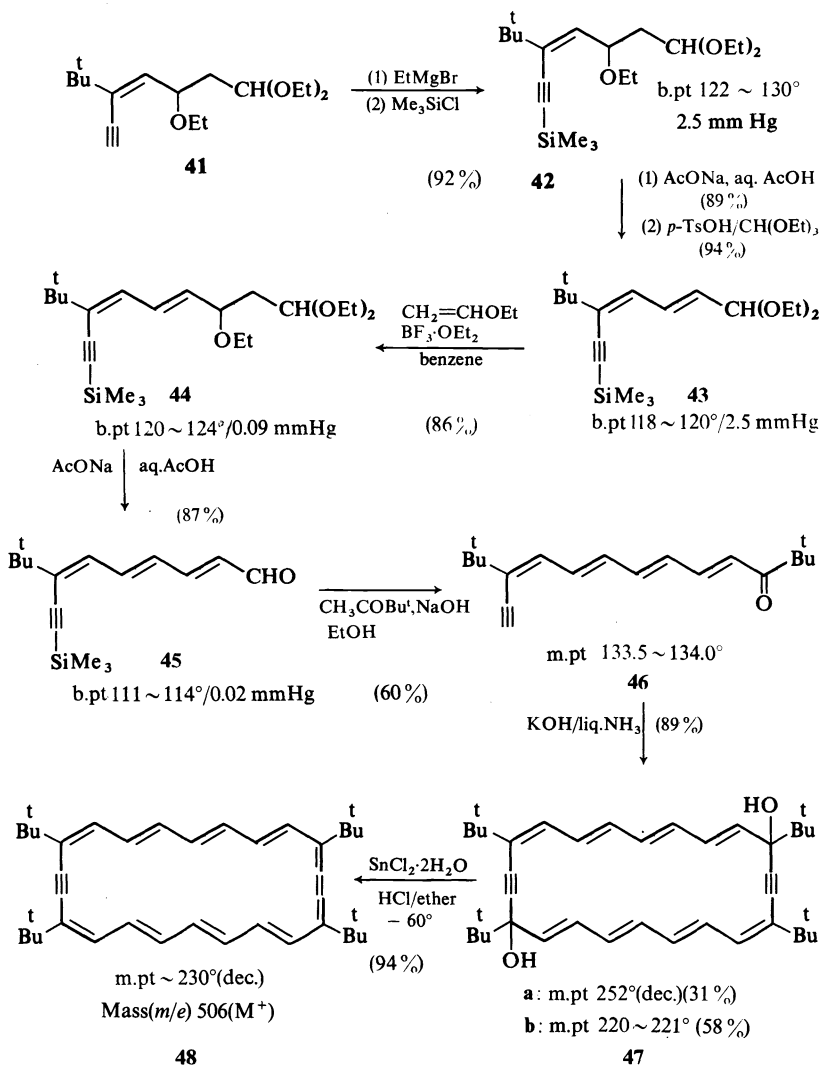|	39		40	
	deep violet cryst.		black violet cryst.	
Outer-H	$-0.21 \sim 0.62$,	m	-0.20, t(H^a); -0.04, d(H^b)	
Ph-H(*o*)	1.33,	m	1.24	d
Ph-H(*m, p*)	2.33,	m	$2.07 \sim 2.80$,	m
t-Bu	7.98,	s		
inner-H	13.28,	m	12.70,	t
60 MHz in CDCl$_3$			100 MHz in THF-d$_8$	

Figure 8. Electronic spectra of tetrasubstituted didehydro[18]annulenes in THF.

(47) was obtained in 89 per cent yield on treatment of the tetraene ketone (46) with potassium hydroxide in liquid ammonia. The cyclic glycol (47) afforded tetra-*t*-butyldidehydro[22]annulene (48) as black violet crystals in 94 per cent yield by dehydroxylative aromatization performed at $-60°$C.

Bu^t—CH=...—CH(OEt)$_2$, OEt, ‖, **41** — (1) EtMgBr / (2) Me$_3$SiCl → Bu^t—...CH(OEt)$_2$, OEt, ‖, SiMe$_3$, **42** (92%), b.pt 122 ~ 130° 2.5 mm Hg

(1) AcONa, aq. AcOH (89%)
(2) p-TsOH/CH(OEt)$_3$ (94%)

Bu^t—...CH(OEt)$_2$, OEt, ‖, SiMe$_3$ **44**
b.pt 120 ~ 124°/0.09 mmHg

← CH$_2$=CHOEt / BF$_3$·OEt$_2$ / benzene (86%) ←

Bu^t—...CH(OEt)$_2$, ‖, SiMe$_3$ **43**
b.pt 118 ~ 120°/2.5 mmHg

AcONa | aq.AcOH (87%)

Bu^t—...CHO, ‖, SiMe$_3$ **45**
b.pt 111 ~ 114°/0.02 mmHg (60%)

→ CH$_3$COBu^t, NaOH / EtOH →

Bu^t—...—Bu^t, ‖, O, **46**
m.pt 133.5 ~ 134.0°

KOH/liq.NH$_3$ (89%)

Bu^t...Bu^t / Bu^t...Bu^t (cyclic) **48**
m.pt ~ 230°(dec.)
Mass(m/e) 506(M$^+$)

← SnCl$_2$·2H$_2$O / HCl/ether / −60° (94%) ←

Bu^t...HO Bu^t / Bu^t...OH Bu^t (cyclic) **47**
a: m.pt 252°(dec.)(31%)
b: m.pt 220 ~ 221° (58%)

As illustrated in *Figure 9*, the didehydro[22]annulene (**48**) exhibits a closely related electronic spectrum with that of tetra-*t*-butyltetradehydro-[22]annulene (**23**, R = *t*-Bu). The n.m.r. spectrum of the didehydro[22]-annulene (**48**) illustrated in *Figure 10* clearly indicates that the [22]annulene (**48**) is still strongly diatropic. As shown in *Table 11*, the n.m.r. spectrum measured at 70°C showed no essential change as compared with that measured at 36°C. This fact indicates high conformational stability of the didehydro-[22]annulene skeleton, because the coalescence temperature of the n.m.r. spectrum of [22]annulene has been reported to be *ca.* 20°C[21].

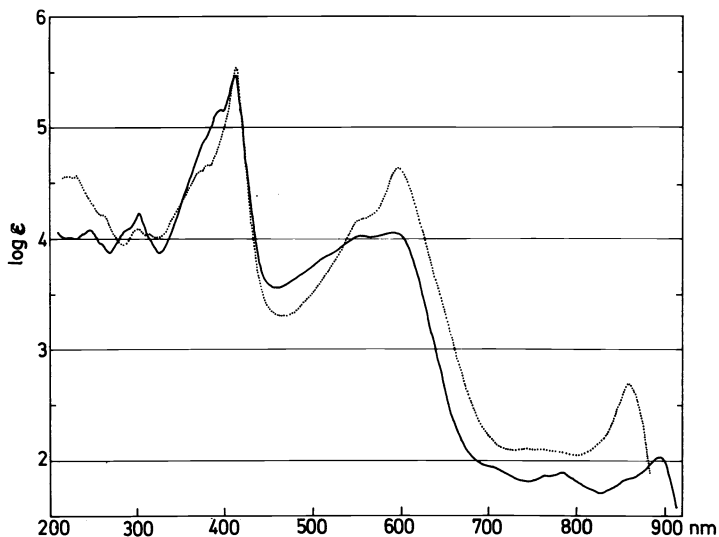The fairly strong diamagnetic ring current observed in tetra-*t*-butyldide-

Figure 9. Electronic spectra of tetra-*t*-butyldidehydro[22]annulene (**48,** ————) and tetra-*t*-butyl-tetradehydro[22]annulene (**23,** R = *t*-Bu,......) in THF.
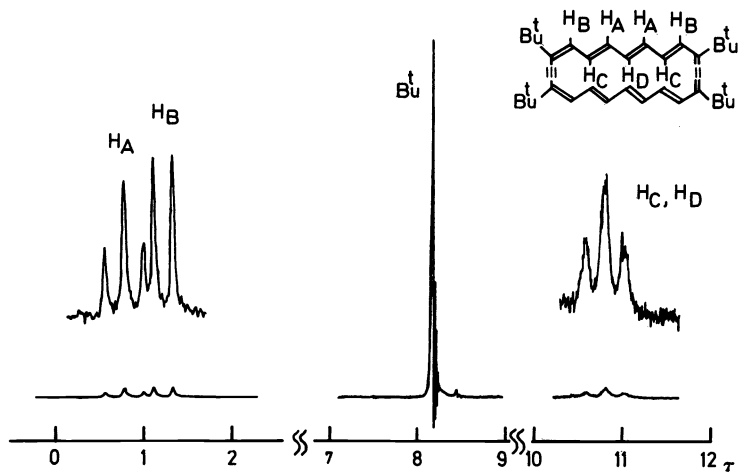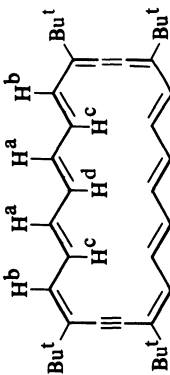

Figure 10. 60 MHz n.m.r. spectrum of tetra-*t*-butyl-didehydro[22]annulene in CDCl$_3$ at 36°C.

hydro[22]annulene (**48**) encouraged us to attempt to prepare didehydro[26]-annulene (**55**)[22].

Trimethylsilyltrienealdehyde (**49,** R = O) used for the preparation of didehydro[22]annulene (**48**) was converted into diethyl acetal [**49,** R = (OEt)$_2$]. Condensation of ethyl vinyl ether with the acetal [**49,** R = (OEt)$_2$]

Table 11. 60 MHz n.m.r. spectra of tetra-t-butyldidehydro[22]annulene in CDCl$_3$ (τ)

Temp, °C	H^a	H^b	t-Bu	H^c, H^d
36	0.79, t 4H	1.24, d 4H	8.18, s 36H	10.82, m 6H
70	0.81, t 4H	1.26, d 4H	8.21, I 36H	10.68, m 6H

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yielded ethoxy acetal (50) as a yellow liquid. Tetraenealdehyde (51) obtained by an acid treatment of the acetal (50) gave crystalline pentaene ketone (52) by the aldol condensation with pinacolone. A diluted solution of the pentaene ketone (52) in tetrahydrofuran was slowly added to a suspension of potassium hydroxide in liquid ammonia to give diastereomers of 26-membered cyclic glycol (54) in a total yield of 93 per cent. It was found that a slow addition of a diluted solution of the ketone (52) is essential to get the

Bu^t ... CHR

SiMe$_3$ **49**

R = O
R = (OEt)$_2$

Bu^t ... CH(OEt)$_2$

OEt

SiMe$_3$ **50**

Bu^t ... Bu^t

O

52

M.pt 92–94°C, Orange cryst.
Overall 41%

Bu^t ... CHO

SiMe$_3$ **51**

Bu^t ... Bu^t

O

Bu^t ... Bu^t

OH

53

Bu^t ... Bu^t HO

Bu^t ... Bu^t

OH

54

Pale yellow cryst.
M.pt 277°C(dec.)(33%)
M.pt 236 C (60%)
Mass(m/e)M$^+$ 592

C$_{42}$H$_{84}$
M.pt 111–113°C (91%)
M$^+$ 588

$\xleftarrow{\text{H}_2}$

Bu^t ... Bu^t

Bu^t ... Bu^t

55

Deep violet cryst.
(89%), (86%)
Mass(m/e) M$^+$ 558

cyclic glycol (54) in a high yield. This fact seems to suggest the intermediacy of ketoalcohol (53) in the cyclic dimerization reaction. Dehydroxylative aromatization of the cyclic glycol (54) performed at − 75°C afforded tetra-

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t-butyldidehydro[26]annulene (**55**) as deep violet crystals in nearly 90 per cent yield from both the diastereomers. Mass spectra of the cyclic glycol (**54**), the [26]annulene (**55**) and the full hydrogenation product ($C_{42}H_{84}$) were found to be consistent with the assigned structures. 100 MHz n.m.r. spectra are illustrated in *Figure 11*. The FT-spectrum is shown at the bottom
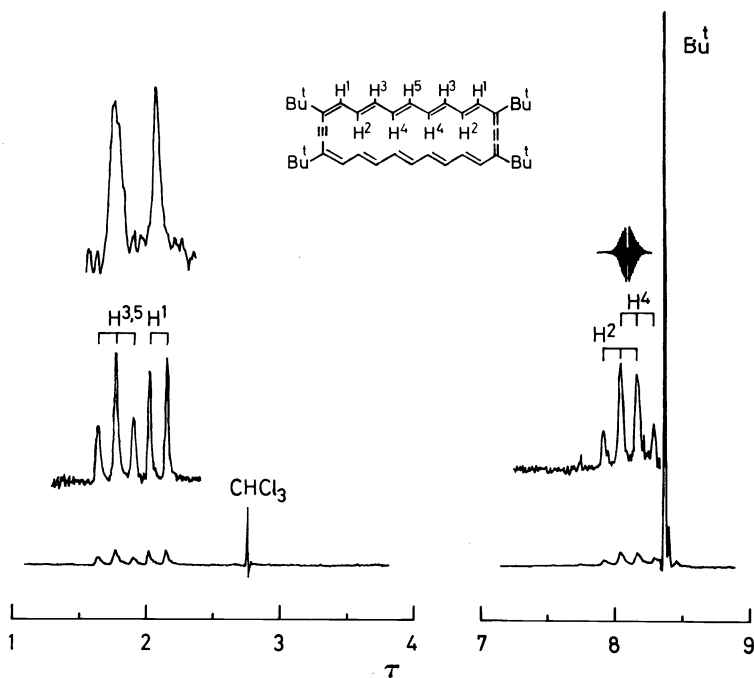
Figure 11. 100 MHz n.m.r. spectra of tetra-t-butyl-didehydro[26]annulene in $CDCl_3$ at 35 °C.

of the figure and the expanded spectrum was recorded above it. Outer protons, H^3 and H^5 gave poorly resolved triplets at τ 1.77, and the outer protons, H^1 showed a doublet at τ 2.07. Inner protons, H^2 and H^4 gave triplets at τ 8.05 and 8.18, respectively. The signal of t-butyl protons appeared at τ 8.39 as a sharp singlet. As recorded at the upper left part of the figure, the pattern of the CW-spectrum of the outer proton region changed markedly on irradiation of the inner proton region. The n.m.r. spectrum indicates that the didehydro[26]annulene (**55**) is still diatropic and the geometry of molecular perimeter is analogous to those of the lower members of this class of didehydro[$4n + 2$]annulenes.

The electronic spectra of didehydro[$4n + 2$]annulenes in tetrahydrofuran are summarized in *Figure 12*. The regular bathochromic shift along with the increase in the ring size is remarkable. Broadening of the absorption curve is notable in the case of didehydro[26]annulene (**55**). The broadening of the absorption curve seems to be attributable to an increase of twisting vibration of the molecular perimeter of the [26] annulene (**55**).
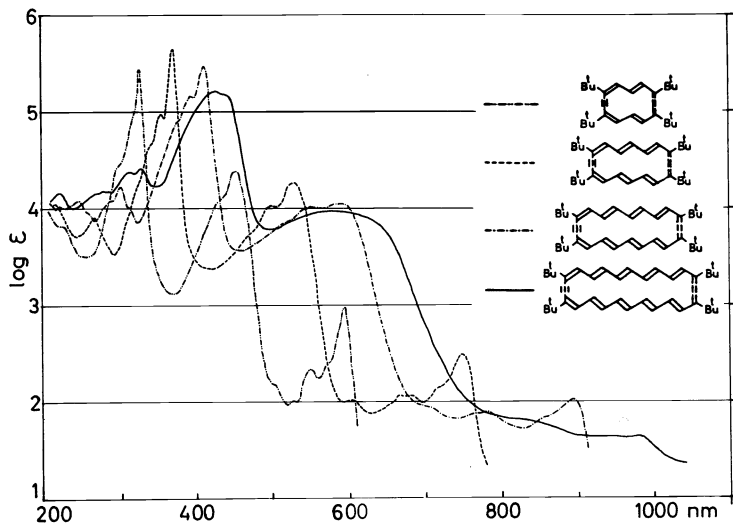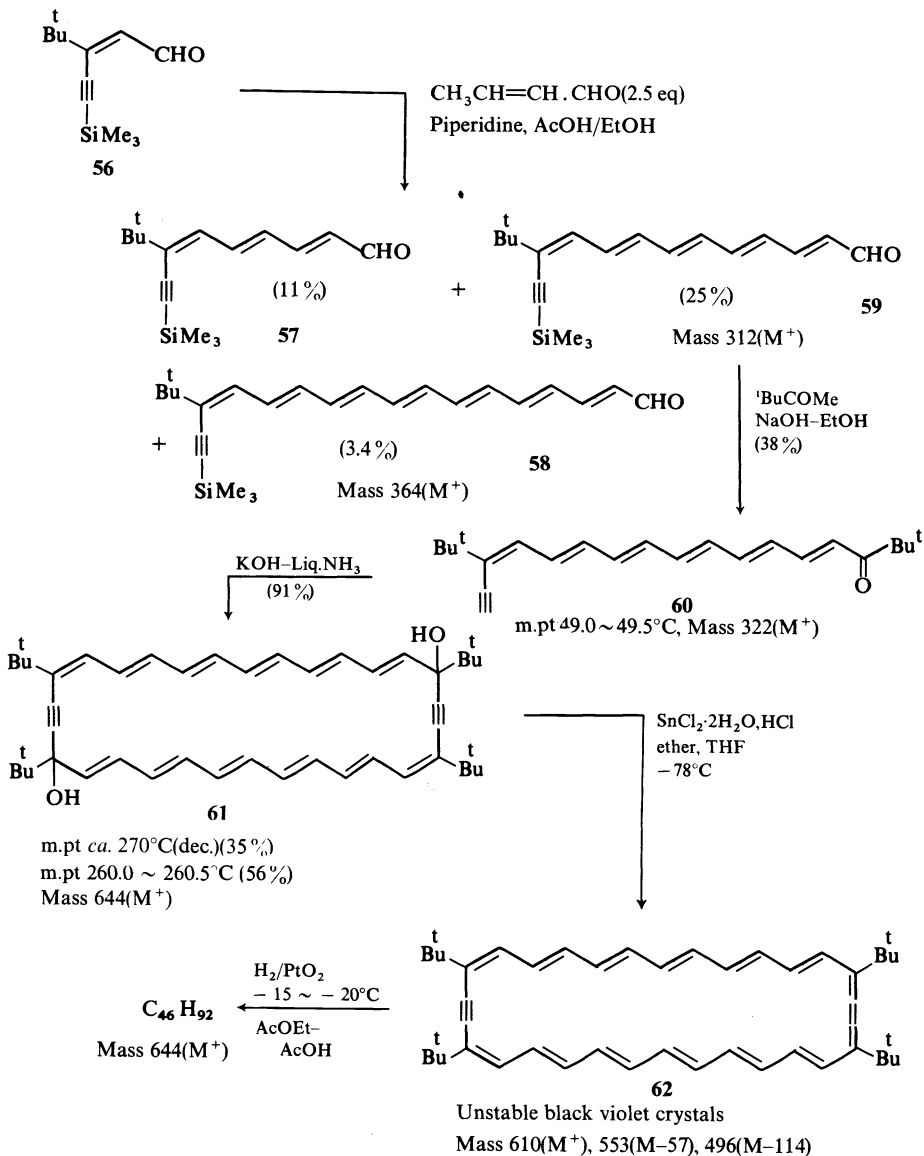
Figure 12. Electronic spectra of didehydro[$4n + 2$]annulenes.

Inspired from the fact that the didehydro[26]annulene (55) is still diatropic, we have carried out the synthesis of tetra-*t*-butyldidehydro[30]-annulene (62)[23]. Because repetition of Isler's reaction seemed to be too tedious to build up the 30-membered ring, we have employed the condensation reaction of crotonaldehyde with 3-*t*-butyl-2-penten-4-ynal.

Trimethylsilylaldehyde (56) dissolved in acetic acid and ethanol containing piperidine was mixed with 2.5 equivalents of crotonaldehyde. The desired pentaenealdehyde (59) was obtained in 25 per cent yield by chromatography of the product on silica gel. Triene- and heptaenealdehydes (57 and 58) were also isolated in 11 and 3.4 per cent yields, respectively. The condensation of the pentaenealdehyde (59) with pinacolone afforded hexaene ketone (60) as unstable orange crystals. Cyclic dimerization of the ketone (60) yielded diastereomeric 30-membered cyclic glycol (61) in a total yield of 91 per cent. Dehydroxylative aromatization of the cyclic glycol (61) at a low temperature yielded tetra-*t*-butyldidehydro[30]annulene (62) as unstable black violet crystals. No satisfactory elemental analyses could be obtained owing to the unstable nature of the [30]annulene (62). However, the molecular ion peak and fragmentation pattern of the mass spectrum were consistent with the assigned structure. The electronic spectrum at $-75°C$ shown in *Figure 13* was obtained using a solution of fresh didehydro[30]-annulene (62) which was prepared from accurately weighed cyclic glycol (61). The ε-values were estimated assuming quantitative conversion of the cyclic glycol (61) into the annulene (62). Just as in the case of didehydro[26]-annulene (55), the didehydro[30]annulene (62) showed a broad and structureless absorption curve.

The 100 MHz FT–n.m.r. spectrum of the didehydro[30]annulene (62)

$$
\overset{t}{Bu}
$$

56

CH₃CH=CH.CHO(2.5 eq)

$CH_3CH=CH \cdot CHO(2.5\ eq)$
Piperidine, AcOH/EtOH

(11%) 57

+ (25%) 59

Mass 312(M⁺)

Mass $312(M^+)$

+ (3.4%) 58

Mass 364(M⁺)

Mass $364(M^+)$

ᵗBuCOMe
NaOH–EtOH
(38%)

^tBuCOMe
NaOH–EtOH
(38%)

60
m.pt 49.0~49.5°C, Mass 322(M⁺)

m.pt $49.0 \sim 49.5°C$, Mass $322(M^+)$

KOH–Liq.NH₃
(91%)

KOH–Liq.NH_3
(91%)

SnCl₂·2H₂O,HCl
ether, THF
– 78°C

$SnCl_2 \cdot 2H_2O$, HCl
ether, THF
$-78°C$

61
m.pt ca. 270°C(dec.)(35%)
m.pt 260.0 ~ 260.5°C (56%)
Mass 644(M⁺)

m.pt ca. $270°C$(dec.)(35%)
m.pt $260.0 \sim 260.5°C$ (56%)
Mass $644(M^+)$

H₂/PtO₂
– 15 ~ – 20°C
AcOEt–
AcOH

H_2/PtO_2
$-15 \sim -20°C$
AcOEt–
AcOH

C₄₆H₉₂

$C_{46}H_{92}$
Mass 644(M⁺)

Mass $644(M^+)$

62
Unstable black violet crystals
Mass 610(M⁺), 553(M–57), 496(M–114)

Mass $610(M^+)$, $553(M-57)$, $496(M-114)$

measured at $-60°C$ is recorded in *Figure 14*. Although some decomposition of the annulene (62) could not be avoided during the measurement, broad multiplets centred at τ 2.50 and also at τ 6.50 could be assigned to outer and inner protons, respectively. t-Butyl protons exhibit a slightly broadened singlet at τ 8.52. The n.m.r. spectrum indicates that the tetra-t-butyldidehydro[30]annulene (62) still sustains a diamagnetic ring current.

Thus, a series of didehydro[4n + 2]annulenes covering a range of 14π-
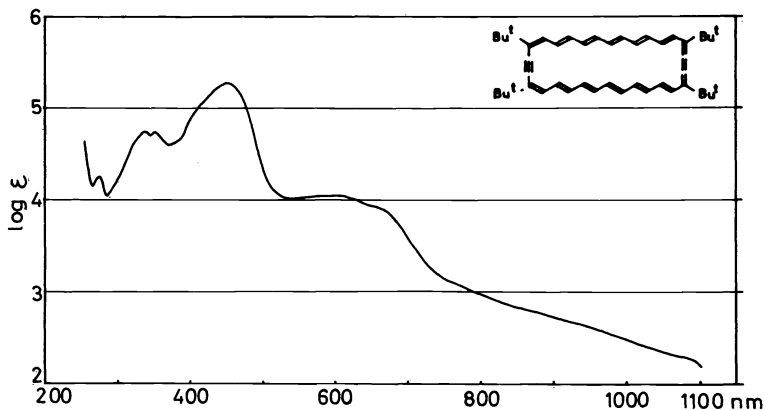
Figure 13. Electronic spectrum of tetra-t-butyl-didehydro[30]annulene.
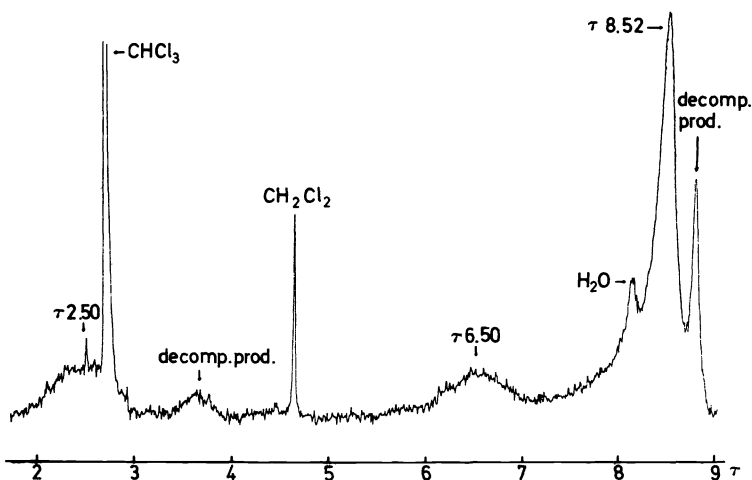
Figure 14. 100 MHz FT-n.m.r. spectrum of tetra-t-butyl-didehydro[30]annulene in CDCl$_3$ at − 60°C.

to 30π-electron system has been prepared. Considering the rather high conformational stability of this class of didehydro[4n + 2]annulenes, it seems reasonable to assume that the didehydroannulenes have approximately the same planarity and essentially the same geometry. Therefore, this series of didehydroannulenes makes it possible to study the effect of ring size on the [4n + 2]π-electron system.

The difference of chemical shift between the signal of inner protons (τ_i) and the lowest field signal of outer protons (τ_o) is summarized in *Table 12*. A progressive decrease of the values of $\tau_i − \tau_o$ along with the increase of ring size is evident.

The chemical shift of the proton of the aromatic compound ($\Delta\sigma$) caused

911

Table 12. The magnitude of chemical shift of tetra-*t*-butyldidehydro[$4n + 2$]annulenes

[$4n + 2$]	Inner protons (τ_i)	Outer protons (τ_o)	Chemical shift $(\tau_i - \tau_o)$
[14]	14.44	0.68	13.76
[18]	13.42	0.13	13.29
[22]	10.83	0.84	9.99
[26]	8.05	1.77	6.28
[30]	6.5	2.5	4.0

in $CDCl_3$.

by the diamagnetic ring current is considered to be proportional to the product of intensity of the ring current (J), the area of the molecule (S) and the inverse-cube distance of the proton from the centre of the ring (R)[24]. As pointed out previously, the outer protons of didehydro[$4n + 2$]annulenes which exhibit signals at the lowest field always locate at the nearest position to the centre of the molecule. Consequently, as shown in *Figure 15*, it seems

$$\Delta\sigma \propto JS/R^3$$

For [14]-, [22]- and [30]-   For [18]- and [26]-
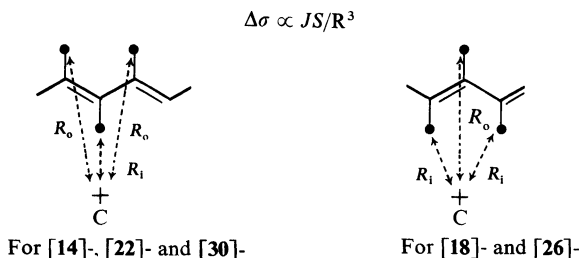
Figure 15. Distance of inner and outer protons from the centre of didehydro[$4n + 2$]annulenes.

not be to absurd to assume that the variation of ring size brings about no great difference of the distance of outer and inner protons from the centre of molecule. Therefore, the value $\tau_i - \tau_o$ divided by the area of corresponding didehydro[$4n + 2$]annulene (S) can be regarded as a quantity directly proportional to the intensity of the ring current (J). The area of hypothetical didehydro[10]annulene was taken as unity being didehydro[14]annulene 2, didehydro[18]annulene 3, and so on. The plots of the values of $\tau_i - \tau_o$ over S against the number of π-electrons gave a smooth curve as illustrated in *Figure 16*. Although the above-stated argument, needless to say, is only an extremely crude approximation, but the theoretical prediction that the bond-alternation in the [$4n + 2$]annulene system should increase along with the increase of n seems to be verified experimentally by the n.m.r. spectral trend of a series of conformationally stable didehydro[$4n + 2$]annulenes. The x-ray structure analysis of tetra-*t*-butyldidehydro[22]annulene (**48**) which is now in progress in the laboratory of Professor Kitahara by Dr Kabuto may offer precious information bearing on increasing bond-alternation along with the increase of ring size.
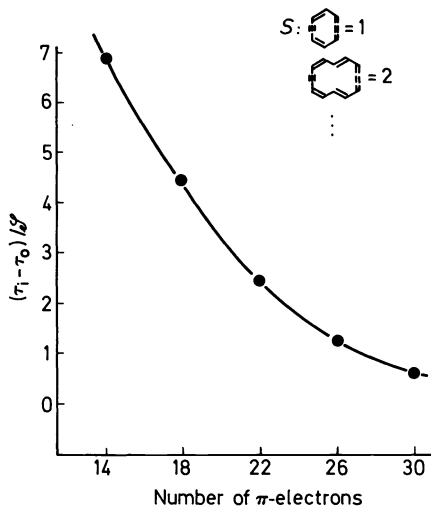
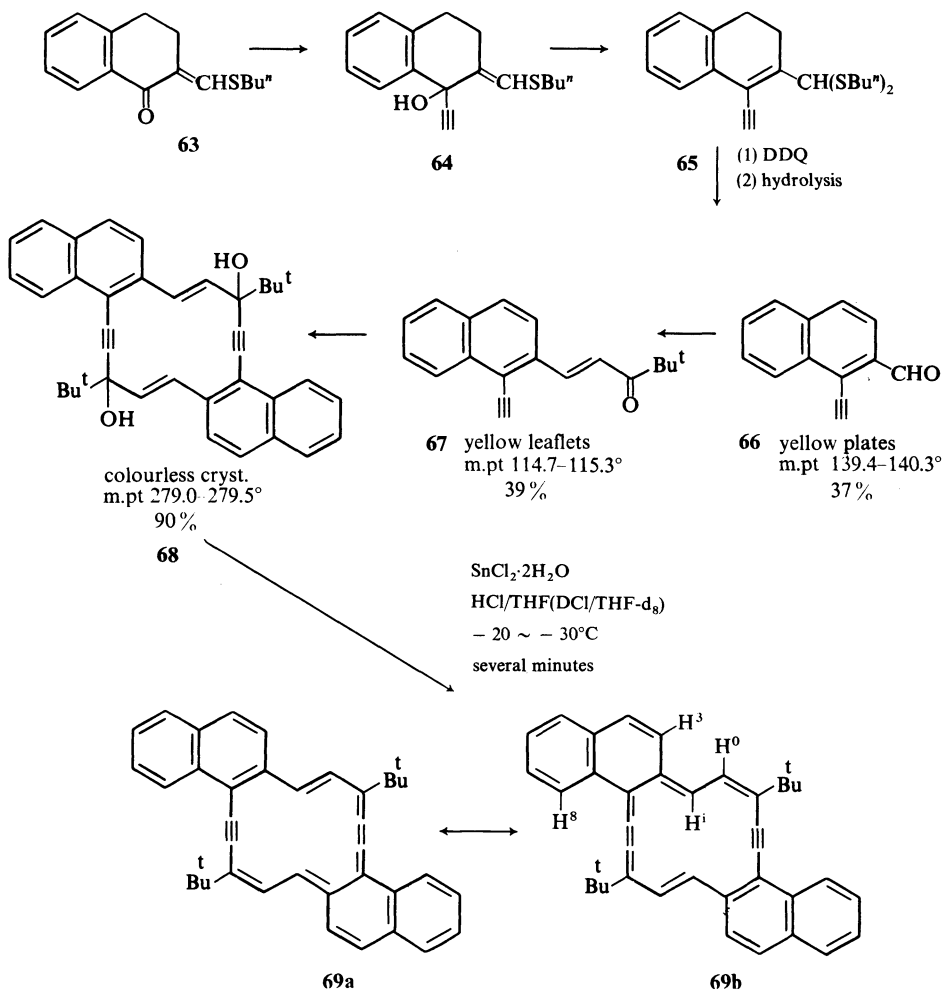*Figure 16*. Decrease of diamagnetic ring current in tetra-*t*-butyl-didehydro[4*n* + 2]annulenes.

ANNELATED DEHYDROANNULENES

Now I would like to turn to our more recent research on annelated annulenes. The properties of [4*n* + 2]annulene annelated with the benzenoid system are of considerable interest with respect to the participation of benzenoid π-electrons in the macrocyclic π-electron system.

The energy required to dispose of one benzene structure in a naphthalene nucleus is smaller than the energy of destruction of benzenoid structure in benzene. On the basis of this naïve consideration, we have carried out in the first place the synthesis of di-*t*-butyl-dinaphthodidehydro[14]annulene (69)[25].

Thioenolether (63) obtained from α-tetralone was converted into ethynyl alcohol (64) by lithium acetylide–ethylenediamine complex[8]. Treatment of the ethynyl alcohol (64) with *n*-butyl mercaptan in the presence of *p*-toluenesulphonic acid yielded ethynyl thioacetal (65) in a high yield. Dehydrogenation of the thioacetal (65) with DDQ followed by hydrolysis with an aqueous acetonitrile containing methyl iodide[26] afforded crystalline 1-ethynyl-2-naphthaldehyde (66). Ethynyl ketone (67) obtained by the aldol condensation of the aldehyde (66) with pinacolone yielded cyclic glycol (68) in a high yield on treatment with potassium hydroxide in liquid ammonia.

Development of an intense blue violet colour could be observed when the glycol (68) was mixed with stannous chloride dihydrate in tetrahydrofuran saturated with hydrogen chloride. The blue violet solution was found to be extremely unstable. If the solution was in contact with air, the colour faded instantaneously even at − 78°C. Therefore, dehydroxylative aromatization of the cyclic glycol (68) was performed under an argon atmosphere employing degassed solvent under the reaction conditions indicated in the scheme. Although all attempts to isolate the product were failures, the formation of

913

63

64

65 | (1) DDQ
(2) hydrolysis

67 yellow leaflets
m.pt 114.7–115.3°
39%

66 yellow plates
m.pt 139.4–140.3°
37%

68

colourless cryst.
m.pt 279.0–279.5°
90%

SnCl$_2$·2H$_2$O
HCl/THF(DCl/THF-d$_8$)
−20 ~ −30°C
several minutes

69a

69b

di-*t*-butyl-dinaphthodidehydro[14]annulene (**69**) could be confirmed on the basis of n.m.r. and electronic spectral evidence.

The 100 MHz n.m.r. spectrum at −54°C measured with a solution of the annelated didehydro[14]annulene (**69**) prepared using deuterium chloride and deuteriotetrahydrofuran is illustrated in *Figure 17*. The doublet at τ 13.45 could be assigned to inner protons. The doublet at τ − 0.22 changed to a sharp singlet on irradiation at τ 13.45. Thus, the low field doublet could be assigned unequivocally to outer protons.

We have also prepared di-*t*-butyl-bis(dihydronaphtho)didehydro[14]-annulene (**70**) as stable dark red needles by a similar sequence of reactions[2]. This compound (**70**) can be regarded as a bis-ethane bridged analogue of the previously mentioned 'para'-isomer of di-*t*-butyl-diphenyldidehydro [14]annulene (**25b**). We have also succeeded in the synthesis of di-*t*-butyl-
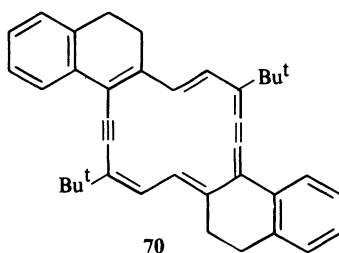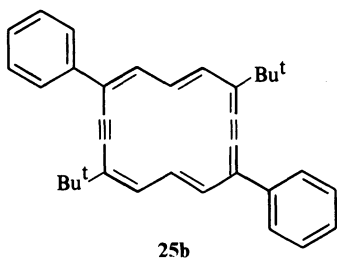
914
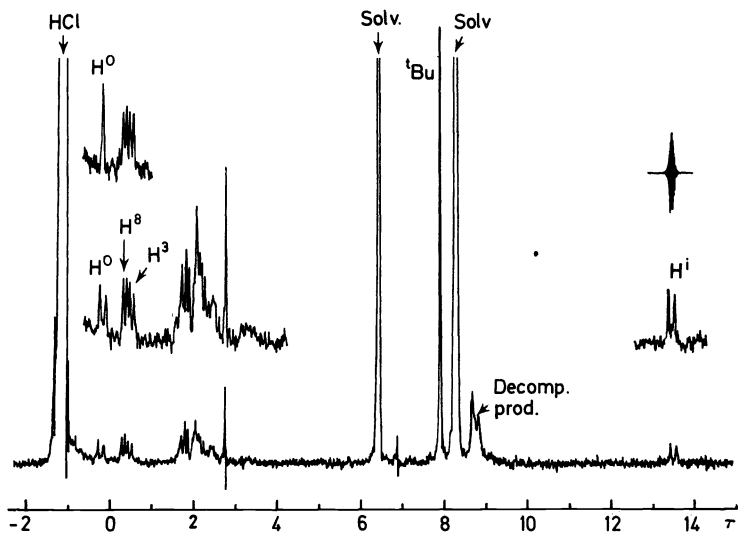
Figure 17. 100 MHz n.m.r. spectra of di-*t*-butyl-dinaphthodidehydro[14]annulene in THF-d$_8$ at − 54°C.

monodihydronaphtho-mononaphthodidehydro[14]annulene (71) as stable dark red crystals. The electronic spectra of di-*t*-butyl-dinaphthodidehydro-[14]annulene (69) and the analogues (70 and 71) are shown in *Figure 18*. The spectrum of the dinaphtho derivative (69) was measured at − 78°C and the ε-values were estimated on the basis of cyclic glycol (68) assuming 100 per cent conversion. The spectra of the analogues (70 and 71) were obtained at room temperature. The n.m.r. spectral data of the dinaphtho
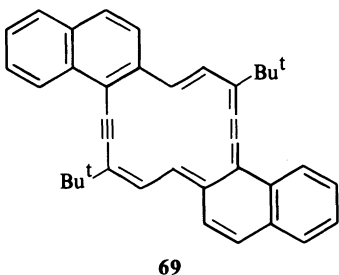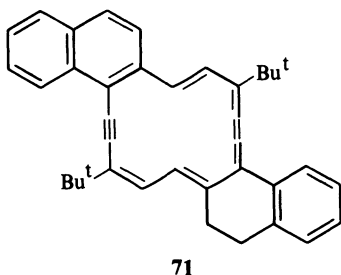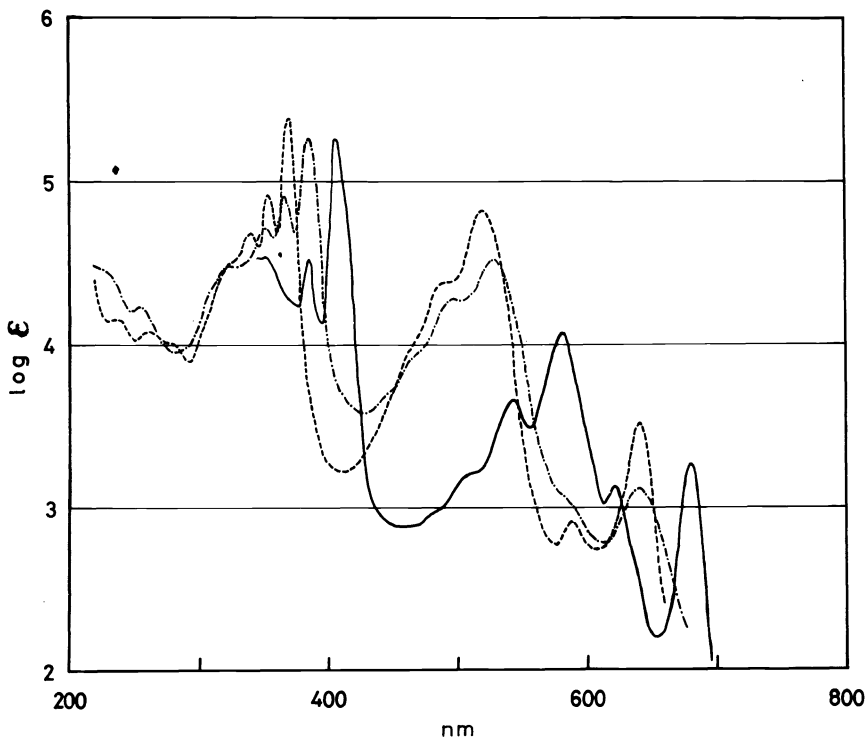
Figure 18. Electronic spectra of di-t-butyl-dinaphthodidehydro[14]annulene and the analogues: dinaphtho derivative (69, ————), mononaphthomonodihydronaphtho derivative (71, —·—·—), and bis(dihydronaphtho) derivative (70, ————).

derivative (69) are compared with those of non-annelated analogues (25b and 70) in *Table 13*. They show closely related n.m.r. spectra. It is especially interesting that the 14π-electron system in the annelated annulene (69) was found to be strongly diatropic as evidenced by the chemical shift of inner and outer protons. As shown in *Table 13*, the values of $\tau_i - \tau_o$ of the annelated annulene (69) were found to be almost the same as those of the reference non-annelated annulenes (25b and 70). The n.m.r. data of unsymmetrically annelated didehydro[14]annulene (71) in which no equivalent Kekulé structures can be written are summarized in *Table 14*. Fairly strong diamagnetic ring current was also observed in the 14π-electron system. However, a marked decrease of the value of $\tau_i - \tau_o$ was found as compared with that of symmetrical dinaphtho-annulene (69).

The difference of properties observed between symmetrical dinaphtho-didehydro[14]annulene (69) and unsymmetrical mononapththo-dide-hydro[14]annulene (71) is extremely interesting. Note that the dinaphtho-annulene (69) sustains a strong diamagnetic ring current comparable to the non-annelated reference annulenes (25b and 70), but the dinaphtho-annulene (69) was found to be highly air sensitive in contrast to the stable reference compounds (25b and 70). By contrast, the less diatropic mononaphtho

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Table 13. 100 MHz n.m.r. spectra of di-t-butyl-dinaphthodidehydro[14]annulene and the non-annelated analogues
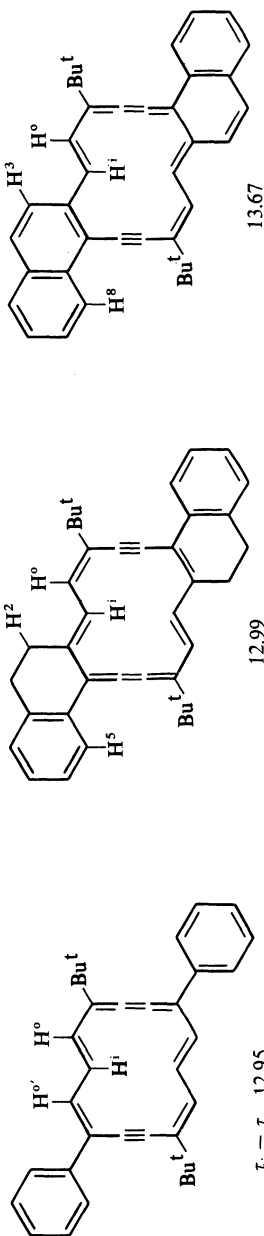
$\tau_i - \tau_o$ 12.95	12.99	13.67
$H^{o'}$ τ 0.12(d) $J = 13.5$	H^o 0.48(d) $J = 14.0$	H^o -0.22(d) $J = 15.0$
H^o 0.47(d) $J = 13.5$	H^i 13.47(d) $J = 14.0$	H^i 13.45(d) $J = 15.0$
H^i 13.42 $J = 13.5$	H^5 1.19(d) $J = 7.5$	H^8 0.29(d) $J = 15.0$
Ph-o 1.35(m)	H^2 5.88(A_2B_2, m)	H^3 0.46(d) $J = 10.0$
Ph-m,p 2.5(m)	t-Bu 8.01(s)	t-Bu 7.89(s)
t-Bu 8.02(s)		
$CDCl_3$, 36°C.	THF-d_8, -55°C.	THF-d_8, -54°C.

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Table 14. 100 MHz n.m.r. spectrum of mononaphthodidehydro[14]annulene in THF-d$_8$ at −52°C
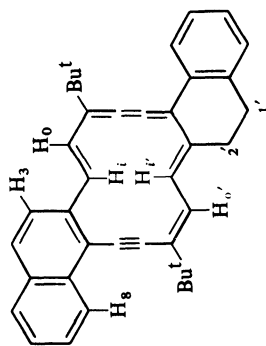
H_o	τ 0.20(d)	$J = 15.0$ Hz
$H_{o'}$	0.83(d)	$J = 13.0$ Hz
H_i	11.22(d)	$J = 15.0$ Hz
$H_{i'}$	11.53(d)	$J = 13.0$ Hz
H_3	0.54(d)	$J = 9.0$ Hz
H_8	0.38(d)	$J = 8.0$ Hz
$H_{2'}$	6.08(m)	
$H_{1'}$	6.68(m)	
t-Bu	8.05(s), 8.09(s)	

$\tau_i - \tau_o$ 11.02

$\tau_{i'} - \tau_{o'}$ 10.70

derivative (71) was found to be stable like the non-annelated analogues (25b and 70). The properties of dinaphtho-annulene (69) reminded us of the properties of polyacene, such as pentacene or hexacene.

For the purpose of gaining further insight into the delocalization of π-electrons in annelated annulene, we synthesized didehydro[14]annulene annelated with benzene[28].

o-Ethynylbenzaldehyde diethyl acetal prepared by the reported method[29] was converted into the lithio derivative (72). Reaction of di-t-butyldieneyne ketone (6, R = R' = t-Bu) with the lithio derivative (72) afforded ethynyl acetal (73). Acid hydrolysis of the acetal (73) followed by the aldol condensation with pinacolone yielded ethynyl ketone (74). The ethynyl ketone (74)
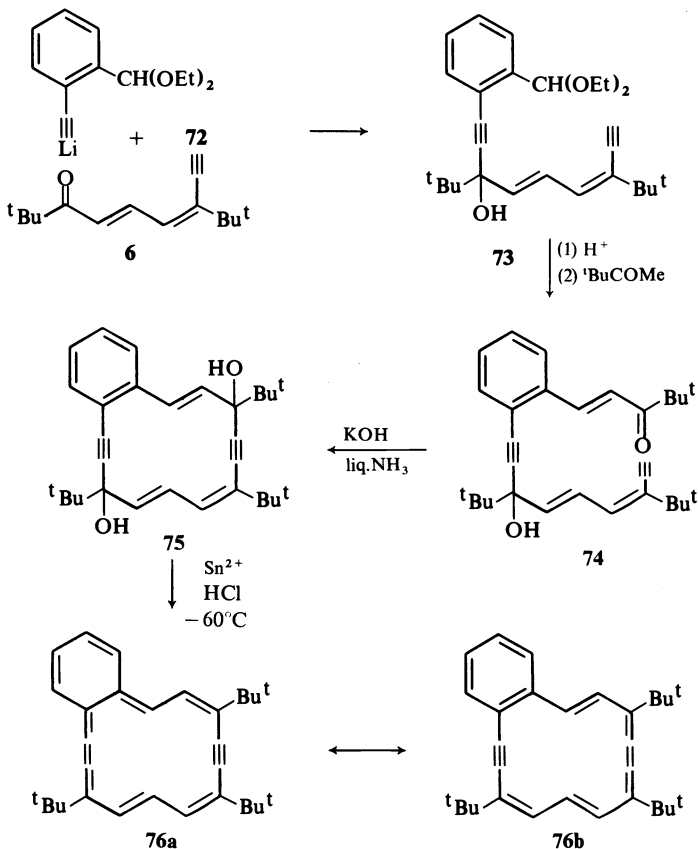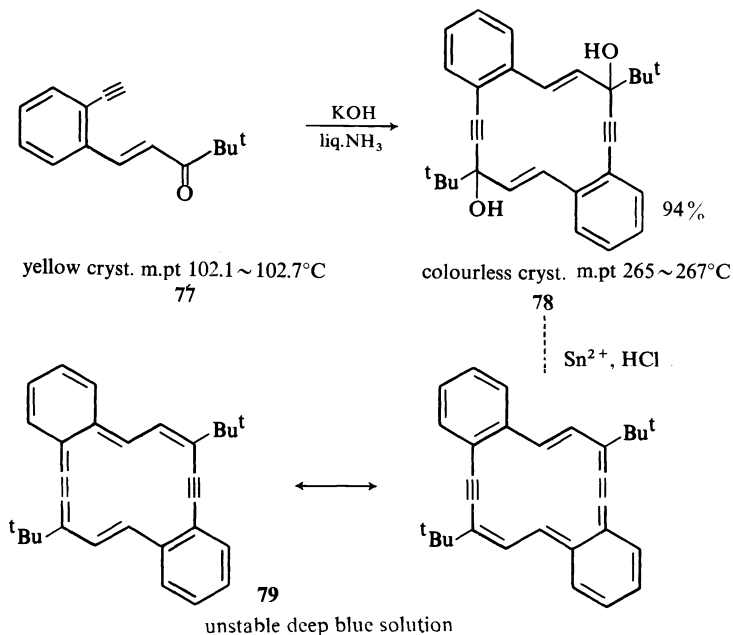

Dark red cryst., M⁺ 396, m.pt 160°C(dec.)

was treated with potassium hydroxide in liquid ammonia to give 14-membered cyclic glycol (75). Dehydroxylative aromatization of crude cyclic glycol (75) afforded benzo-tri-t-butyldidehydro[14]annulene (76) as dark red crystals. The n.m.r. spectral parameters are summarized in *Table 15*.

Table 15. 100 MHz n.m.r. spectrum of benzo-tri-*t*-butyldidehydro[14]annulene in THF–d_8 at 35°C
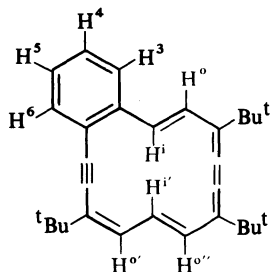
$H^{i\prime}$	τ 9.29,	dd,	$J = 12.0$,	14.5 Hz
H^i	9.19,	d,	$J = 15.5$	
t-Bu	8.30,	s,		
H^4, H^5	2.26,	m,		
$H^{o\prime\prime}$	1.70,	d,	$J = 14.5$	
$H^{o\prime}$	1.67,	d,	$J = 12.0$	
H^3	1.48,	dd,	$J = 2.0$,	7.5
H^o	1.03,	d,	$J = 15.5$	
H^6	0.92,	dd,	$J = 2.5$,	8.0

$\tau_i - \tau_o = 8.16$; $\tau_{i\prime} - \tau_{o\prime} = 7.62$; $\tau_{i\prime} - \tau_{o\prime\prime} = 7.59$

It is clear that the 14π-electron system in the benzo-annelated annulene (**76**) sustains a considerable diamagnetic ring current. However, the values of $\tau_i - \tau_o$ (τ 8.16, 7.62 and 7.59) were found to be much less than that of the mononaphtho analogue (**71**, τ 10.67).

yellow cryst. m.pt 102.1∼102.7°C
77

colourless cryst. m.pt 265∼267°C
78

Sn²⁺, HCl

79
unstable deep blue solution

920

In view of the unstable nature of dinaphtho-didehydro[14]annulene (**69**) in spite of the strong diamagnetic ring current in the 14π-electron system, dibenzodidehydro[14]annulene (**79**) was anticipated to be more unstable than the monobenzo derivative (**76**). *t*-Butyl ketone (**77**) prepared by the aldol condensation of pinacolone with 2-ethynylbenzaldehyde afforded dibenzo 14-membered cyclic glycol (**78**) in a high yield on treatment with potassium hydroxide in liquid ammonia. Dehydroxylative aromatization of the glycol (**78**) performed under an argon atmosphere at a low temperature afforded a deep blue solution. Expectedly, the solution was found to be extremely unstable, and the measurements of electronic and n.m.r. spectra have not yet been achieved[30].

With the purpose of increasing the stability of annelated annulene, we have prepared benzonaphtho-di-*t*-butyl-didehydro[14]annulene (**85**)[31].

The reaction of the lithio derivative of 2-ethynylbenzaldehyde diethyl acetal (**72**) with dihydronaphthylvinyl ketone (**80**)[27] afforded hydroxy acetal
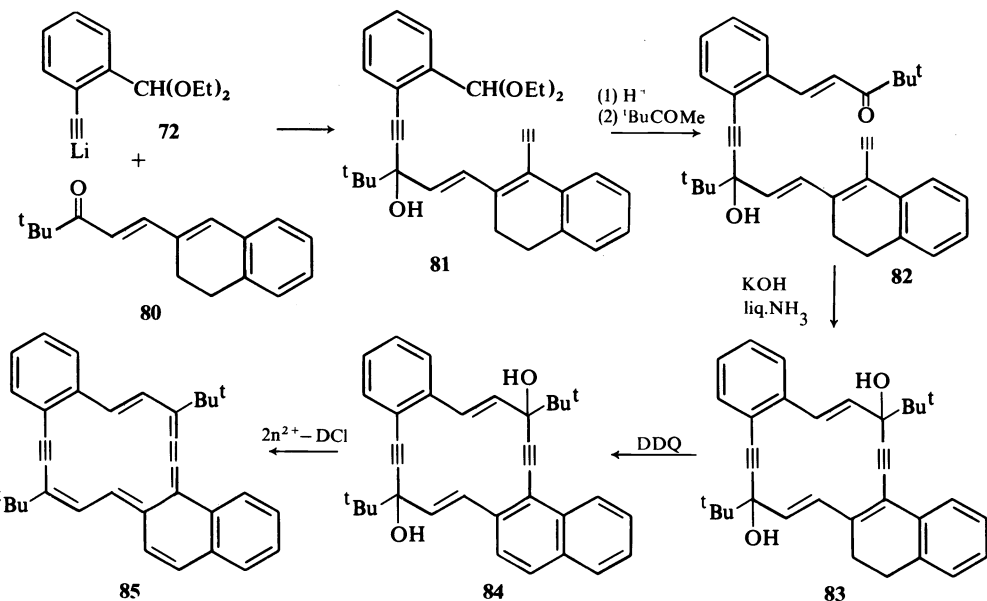
(**81**). Aldehyde obtained by acid hydrolysis of the acetal (**81**) was converted into ethynyl ketone (**82**) by the condensation with pinacolone. The ethynyl ketone (**82**) was treated with potassium hydroxide in liquid ammonia to give cyclic glycol (**83**). Dehydrogenation of the cyclic glycol (**83**) with DDQ afforded cyclic glycol containing a benzene and a naphthalene nucleus (**84**). Dehydroxylative aromatization of the cyclic glycol (**84**) at a low temperature gave an unstable deep violet solution. As illustrated in *Figure 19*, the electronic spectrum measured at $-78°C$ using the violet solution was found to be closely related with that of the dinaphthodidehydro[14]annulene (**69**), thus indicating the formation of benzonaphthodidehydro[14]annulene
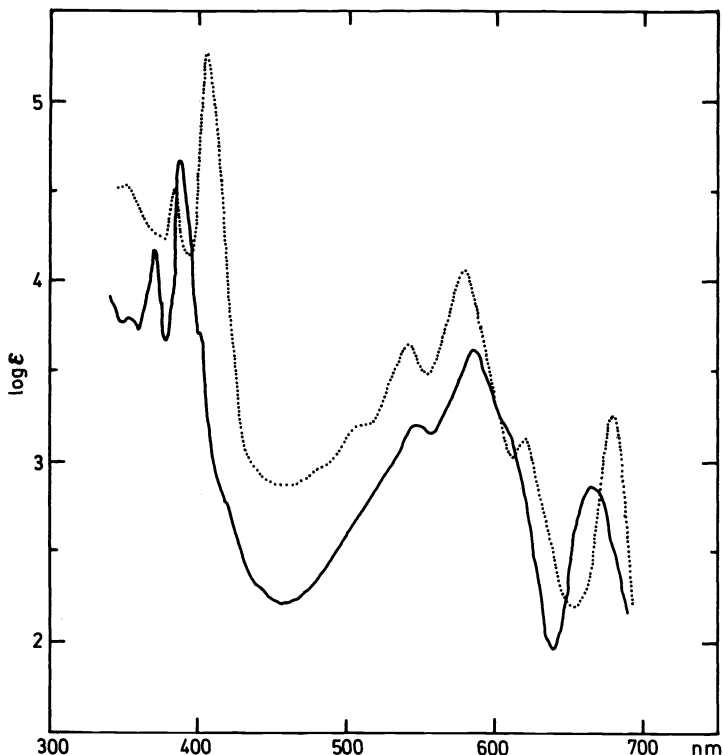
921

Figure 19. Electronic spectra of benzonaphtho-di-*t*-butyl-didehydro[14]annulene (**85**, ————)
and dinaphtho-d-*t*-butyl-didehydro[14]annulene (**69**, ...).

(**85**). Preliminary measurement of n.m.r. spectrum of the annelated annulene (**85**) prepared in deuteriotetrahydrofuran using deuterium chloride gave a poor spectrum owing to decomposition of the annelated annulene (**85**). However, signals attributable to the annelated annulene (**85**) could be observed. The signals at τ *ca.* 0.15 and 0.50 could be assigned to outer protons, and those of τ *ca.* 12.05, 8.11 and 8.01 could be assigned to inner and *t*-butyl protons, respectively.

Although experiments to obtain a clear n.m.r. spectrum are now under way, the $\tau_i - \tau_o$ and $\tau_{i'} - \tau_{o'}$ values of benzonaphthodidehydro[14]-annulene (**85**) could be tentatively estimated to be τ 11.90 and τ 11.55. As summarized in *Table 16*, the values of $\tau_i - \tau_o$ and $\tau_{i'} - \tau_{o'}$ are larger than those of the monobenzo- (**76**) and mononaphtho- (**71**) analogues and smaller than that of dinaphtho-annulene (**69**).

Our studies on annelated annulenes are still in an early stage. But the few results obtained seem to suggest that the difference of resonance energies between annulene ring and benzenoid nucleus governs the magnitude of π-electron delocalization in the annulene system, and whether equivalent Kekulé structures can or cannot be written exerts significant effect on the degree of delocalization of π-electrons in the annulene system.

Table 16. The magnitude of chemical shift of annelated didehydro[14]annulenes

	$\tau_i - \tau_o$	$\tau_{i'} - \tau_{o'}$
Monobenzo-	8.16	7.62
Mononaphtho-	11.02	10.70
Benzonaphtho-	11.90	11.55
Dinaphtho-	13.67	—

Further studies on didehydro[18]annulene annelated with naphthalene which are now in progress may offer further information on the characteristics of annelated annulenes.

To summarize, we have synthesized a series of tetradehydro[$4n + 2$]-annulenes ($n = 4$ and 5], a series of didehydro[$4n + 2$]annulenes ($n = 3, 4, 5, 6$ and 7) and a few annelated didehydro[14]annulenes. Studies on these conformationally stable dehydroannulenes have brought forth some fundamental aspects on π-electron delocalization. Of course, a number of problems await further investigations. For instance, the condensed system of diatropic annulene consisting of the same ring size corresponding to naphthalene remains to be accomplished.

ACKNOWLEDGEMENT

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