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SYNTHESES AND PROPERTIES OF BENZANNELATED DIPHENYLPENTADECAFULVENE DERIVATIVES

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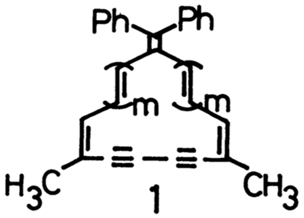
Synthesis of 10-methyl-16,16-diphenyl-4,5-benzo-6,8-bisdehydro- **4**, 12-methyl-16,16-diphenyl-6,7-benzo-8,10-bisdehydro- **5**, and 16,16-diphenyl-4,5:10,11-dibenzo-6,8-bisdehydropentadecafulvene **6** has been described. Comparison of ^{1}H-NMR spectra of these benzannelated fulvenes **4**-**6** with that of nonbenzannelated fulvene **3** reveals that 5,10-dimethyl-16,16-diphenyl-6,8-bisdehydropentadecafulvene **3** is atropic.

Of many methods available for synthesis of fulvene system, most involve either addition reaction followed by elimination, or condensation reaction between various reagents and cyclic compounds to elaborate an exocyclic double bond.[1] However, we recently reported a synthesis of diphenyltrideca- (type **1**: m=1), -pentadeca- (type **2**: m=1, **3**), -heptadeca- (**1**: m=2), and -nonadecafulvene derivative (**2**: m=2) by an intramolecular oxidative coupling from the corresponding cross-conjugated acyclic polyenes containing two terminal acetylene groups. This method is advantageous since the precursors of the desired fulvenes would serve as the "open chain" models necessary for investigation of ring currents. Furthermore, although the fulvenes of both types **1** and **2** were suggested to be atropic by an examination of their ^{1}H-NMR spectra,[2] an uncertainty was left in that judgement of tropicity of type **2**, particularly of diphenylpentadecafulvene **3**, since the inner (H^B, $H^{A'}$, $H^{D'}$) protons of **3** resonate at an unusually low field, whereas the outer (H^A, H^C, $H^{B'}$, $H^{C'}$, $H^{E'}$) and methyl protons of **3** do at a rather high field. Thus, we kept our mind on a question that the cross-conjugated 16π-electron system **3** might be paratropic.



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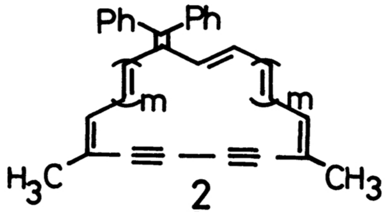

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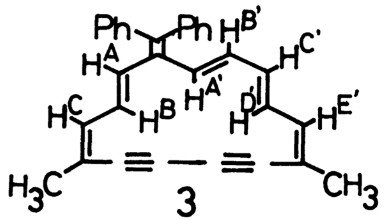

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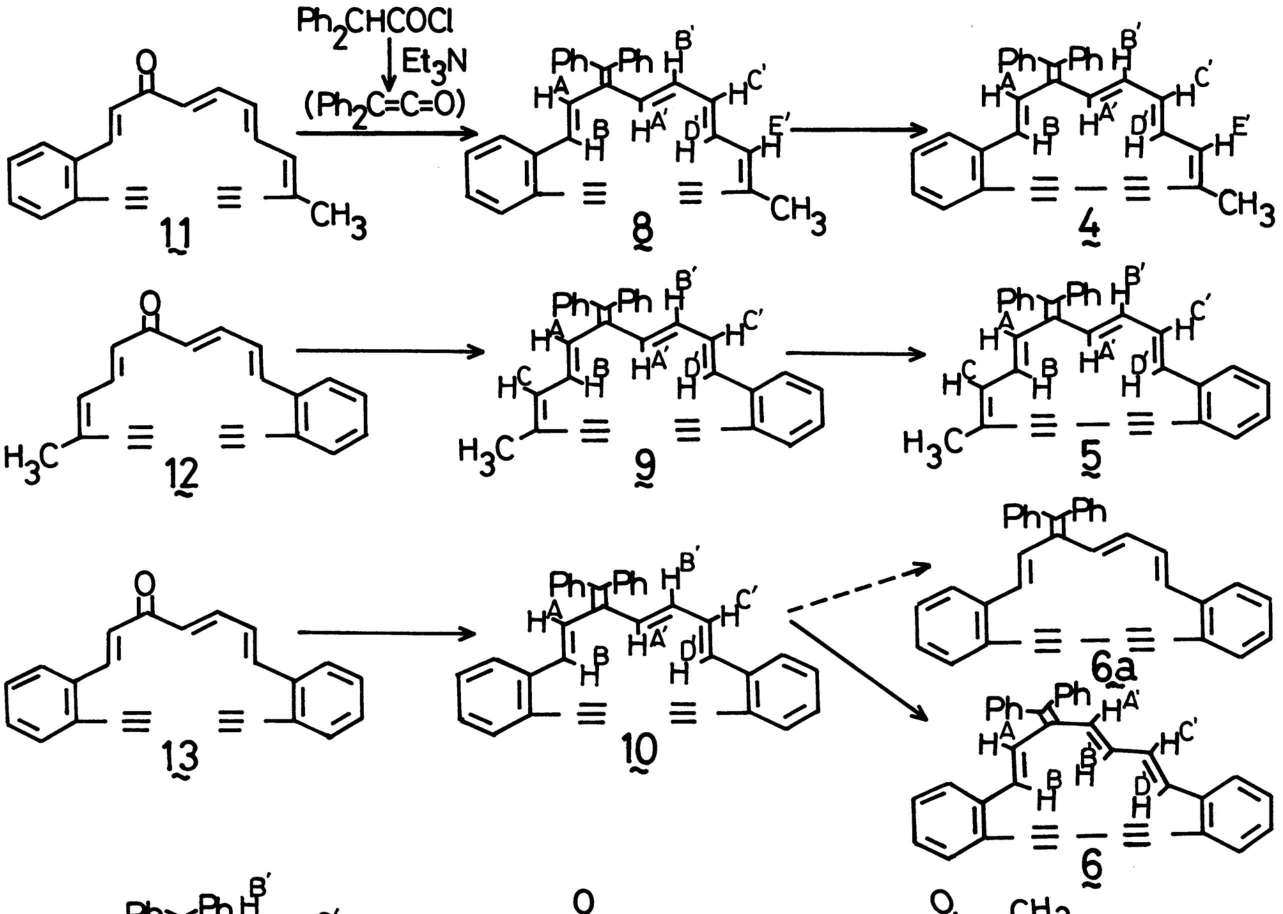
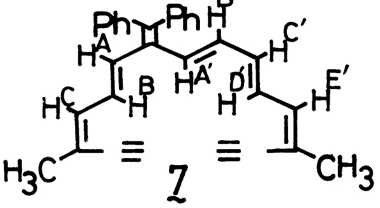
It is well recognized that annelation of one or more benzenoid rings for a large-membered conjugated π-electron system usually causes progressive reduction of tropicities of the macrocyclic system with an increasing annelation if the position of benzenoid rings excludes the contribution of an equivalent Kekulé structure.[3,4] Accordingly, we considered that an inspection on the tropicity of the benzannelated series of **3** would provide an alternative diagnostic tool for judgement of tropicity of **3** itself.

In order to get a further insight for the tropicity of **3** as well as to test the scope of validity of the reaction sequence used for the syntheses of the previously reported fulvene derivatives,[2] we were interested in examining the properties of the benzannelated derivatives of **3**. In this paper, we now describe syntheses and properties of the title compounds 4-6, as well as the further examination of the properties of 3.

The synthesis was accomplished by the reaction sequence similar to that adopted for compounds of types 1 and 2,2) and we have obtained the objective fulvenes in moderate yields. Thus, the reaction of 1-(o-ethynylphenyl)-9-methyl-1,4,6,8-undecatetraen-10-yn-3-one (11),4b) 1-(o-ethynylphenyl)-9-methyl-1,3,6,8-undecatetraen-10-yn-5-one (12),4b) and 1,7-bis(o-ethynylphenyl)-1,4,6-heptatrien-3-one (13),4b) with diphenylketene5) formed *in situ* from diphenylacetyl chloride and triethylamine in dry benzene at room temperature for 20-25 h afforded 11-(o-ethynylphenyl)-3-methyl-9-(diphenylmethylene)-3,5,7,10-undecatetraen-1-yne (8, yellow needles, mp. 134-135°C, 38%),6) 11-(o-ethynylphenyl)-3-methyl-7-(diphenylmethylene)-3,5,8,10-undecatetraen-1-yne (9, yellow needles, mp. 143-144°C, 34%), and 1,7-bis(o-ethynylphenyl)-3-(diphenylmethylene)-1,4,6-heptatriene (10, pale yellow needles, mp. 170-171°C, 54%), respectively. Oxidative coupling of 8, 9, and 10 with anhydrous copper(II) acetate in pyridine and dry ether at 50°C7) gave 10-methyl-16,16-diphenyl-4,5-benzo-6,8-bisdehydro- (4, orange plates, mp. 174-175°C, 65%), 12-methyl-16,16-diphenyl-6,7-benzo-8,10-bisdehydro- (5, yellow needles, mp. 177-178°C, 46%), and 16,16-diphenyl-4,5:10,11-dibenzo-6,8-bisdehydropentadecafulvene (6, pale yellow needles, mp. 175-176°C, 68%), respectively.

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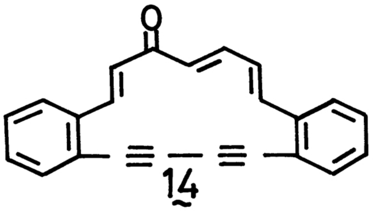
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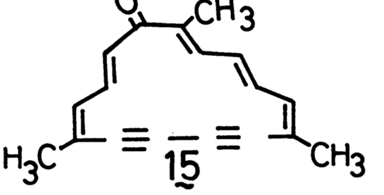
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The ^1H-NMR spectral data of these fulvenes 3-6 as well as those of the acyclic compounds 7-10 are

Table 1. The ^{1}H-NMR Chemical Shifts of the Compounds 3–10 in CDCl$_3$ at 200 MHz (τ-Values)

Compd.	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	$H^{D'}$	$H^{E'}$	CH_3	Ph H	-C≡CH
7[a]	3.65	3.63	3.03	3.31	3.67	3.68	3.33	3.67	8.07	2.69–2.88	6.68, 6.72
3[a]	3.61	2.64	2.24	4.15	3.60	3.93	2.40	3.57	8.20	2.7–2.9	
Δ(3-7)	-0.04	-0.99	-0.79	+0.84	-0.07	+0.25	-0.93	-0.10	+0.13		
8	3.13	3.54	2.57	3.09		3.64	3.25	3.64	8.06	2.47–2.84	6.66
4	3.00	(2.60–2.94)	2.25	4.11		3.69	(2.60–2.94)	3.52	8.16	(2.60–2.94)	
9	3.61	3.52	2.95	(2.37–3.24)	3.63	3.59	(2.37–3.24)		8.05	(2.37–3.24)	6.65, 6.70
5	(3.36—	—3.56)	2.47	(3.36—		—3.56)	(2.61–2.86)		8.15	(2.61–2.86)	
10	3.11	3.44	2.51	2.95		3.06	(2.36–2.84)			(2.36–2.84)	6.62, 6.68
6	3.00	3.32	2.38	3.59		3.33	3.09			2.60–2.91	

a) See ref. 2).

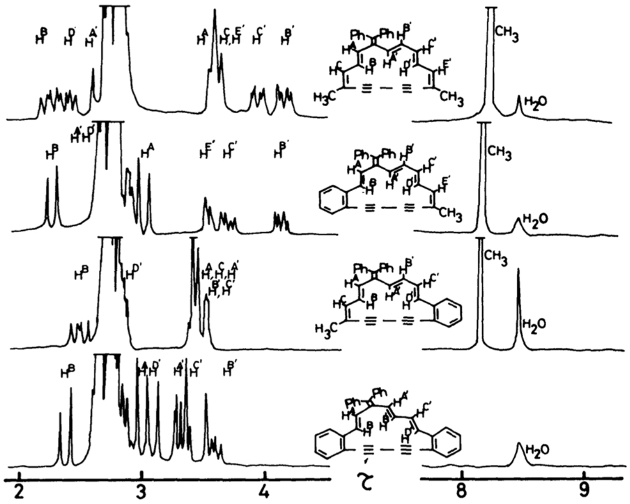

Fig. 1. The ^{1}H-NMR spectra of fulvenes in CDCl$_3$

listed in Table 1. Individual assignments were made on the basis of multiplicities and coupling constants, and were clarified by the decoupling experiments where possible and necessary.

Comparison of the ^{1}H-NMR chemical shifts of the various protons of the benzannelated fulvenes 4–6 with those of the corresponding acyclic compounds 8–10, respectively, indicates that the fulvenes 4–6 are atropic, since no significant upfield and downfield shift due to the outer and inner protons, respectively, are observed as compared with those of the corresponding acyclic compounds. This is readily seen from Figure 1 which shows the ^{1}H-NMR spectra of 3–6 at room temperature. In the spectra of the benzannelated fulvenes 4–6, compared with that of 3, the high- and low-field shifts of the resonances of the outer and inner protons, respectively, are not observed. However, as exemplified in the spectrum of the monobenzannelated fulvene 4, the inner H^B and the outer $H^{B'}$, $H^{C'}$, $H^{E'}$ protons resonate at almost the same region as those of nonbenzannelated fulvene 3. As to only the inner H^B proton, the similar tendency is true even in the spectra of the benzannelated fulvenes 5 and 6. Thus, decreasing of both the high- and low-field shifts due to the outer and inner protons, respectively, is not clearly observed on passing from nonbenzannelated 3 to dibenzannelated 6 *via* monobenzannelated fulvenes 4 and 5. Since a decrease in tropicity by benzannelation was found to be true for the corresponding 14π-electron, diatropic bisdehydro[15]annulenone series[4)] which should have geometry similar to these fulvene systems, this observation obtained from the ^{1}H-NMR spectra of the fulvenes together with an examination of the comparison of the chemical shifts of the corresponding acyclic model 7,[2)] leads us to believe that an appearance of the resonances due to the outer and inner protons at a rather high- and low-field, respectively, in the spectrum of 3 does not reflect a paramagnetic ring current induced in 16π-electron, cross-conjugated system of 3. The ^{1}H-NMR spectral pattern observed for 3 must be a reflection of the fact that the anisotropies of two phenyl and diacetylene moieties are at work. Thus, it is concluded that the fulvene 3 is not paratropic, but is atropic.

In addition, in rather surprisingly contrast to the cases of 3-5, the dibenzannelated fulvene does not exist in a conformation 6a, but in 6 at room temperature.[8)] This follows from the fact that the value of $J_{B',C'}$ is 10 Hz, pointing to an s-*trans* relationship of the $CH^{B'}$, $CH^{C'}$ bond.

Since the bisdehydro[15]annulenone ring has been found to have very high planarity of the molecular skeleton among the similar type bisdehydroannulenone systems[9)] and the corresponding dibenzannelated bisdehydro[15]annulenone was shown to exist in a conformation 14, changing from an oxygen atom of the annulenone to bulky phenyl groups at C_{16}-position of the fulvene must arouse an unlikely conformation 6. One possible explanation for this result is that in cases of 3-5, the steric hindrance experienced between the two phenyl groups and the neighboring olefinic protons can be relieved over the whole of a rather flexible, nonbenzannelated or monobenzannelated molecular skeleton. On the other hand, the molecular skeleton of 6, which is made to less flexible system than those of 3-5 by the fusion of two benzene rings, can not relieve the hindrance, causing the conformational change. The conformation of 6 is structually relevalent to that of the corresponding bisdehydro[15]annulenone 15 carrying a methyl group at C_{14}-position.[4)]

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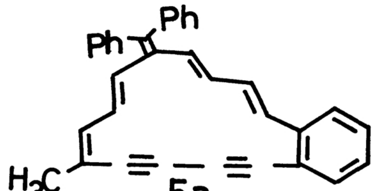

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