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# PROPERTIES OF BENZANNELATED TRISDEHYDRO[10.10.2][14]ANNULENO[14]ANNULENES

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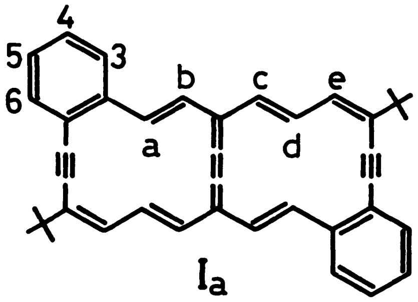
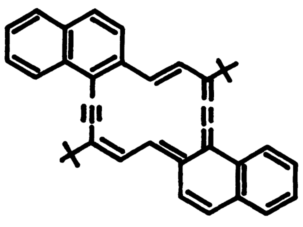
Increase of diatropicity of the dibenzotrisdehydro[14]annuleno-[14]annulene as compared with that of benzotrisdehydro[14]annuleno-[14]annulene, which is expected if the dibenzannulenoannulene is a peripheral conjugated system, could not be observed. The observed NMR behavior seems to indicate that the dibenzo derivative is a fused system consisting of two 14π-electron systems.

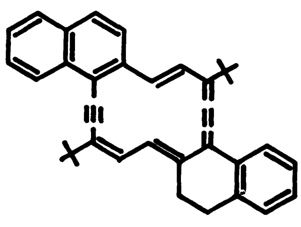
Both of the dibenzo-di-*t*-butyl- (I) and benzo-tri-*t*-butyltrisdehydro-[10.10.2][14]annuleno[14]annulenes (II)1) were found to be stable compounds. It is to be noted that the dibenzo derivative (I) shows almost the same stability as the monobenzo analogue (II), whereas the dinaphthobisdehydro[14]annulene (III)2) has been found to be highly unstable in contrast to the stable mononaphtho derivative (IV).3) The dibenzo- (I) and benzo derivatives (II) gave 1:1 CT complexes with



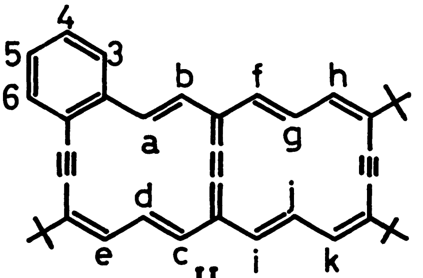
Ia



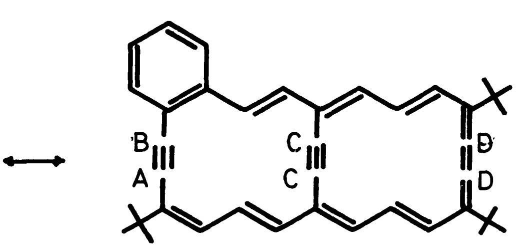
III



IV



IIa



IIb

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2,4,7-trinitro-9-fluorenone, dark bluish green crystals, mp 275°C (dec.) and greenish black crystals, mp > 280°C, respectively.

As illustrated in Fig., the annelated annulenoannulenes (I and II) showed closely related electronic spectra with that of parent trisdehydro[14]annuleno-[14]annulene (V).[4] However, an interesting shift of absorption maxima was observed, *i.e.*, the longest wavelength $^1L_b$ band[5] showed progressive hypsochromic shift with hyperchromism passing from V to I *via* II, and on the contrary the medium wavelength $^1L_a$ and the short wavelength $^1B$ bands exhibited bathochromic shift being much larger in the $^1L_a$ band.

The $^1H$ NMR parameters are summarized in Table together with those of benzo-tri-*t*-butylbisdehydro[14]- (VI),[6] tetra-*t*-butylbisdehydro[14]annulenes (VII)[7] and the non-annelated trisdehydro[14]annuleno[14]annulene (V). As reported in previous papers,[2,3] the diatropicity of the dinaphthobisdehydro[14]annulene (III) was found to be much stronger than the naphtho-dihydronaphtho analogue (IV), which does not possess equivalent Kekulé structures. If the dibenzotrisdehydro-[14]annuleno[14]annulene (I) is a peripheral 22π-electron system, an appreciable enhancement of diatropicity should be observed as compared with the monobenzo

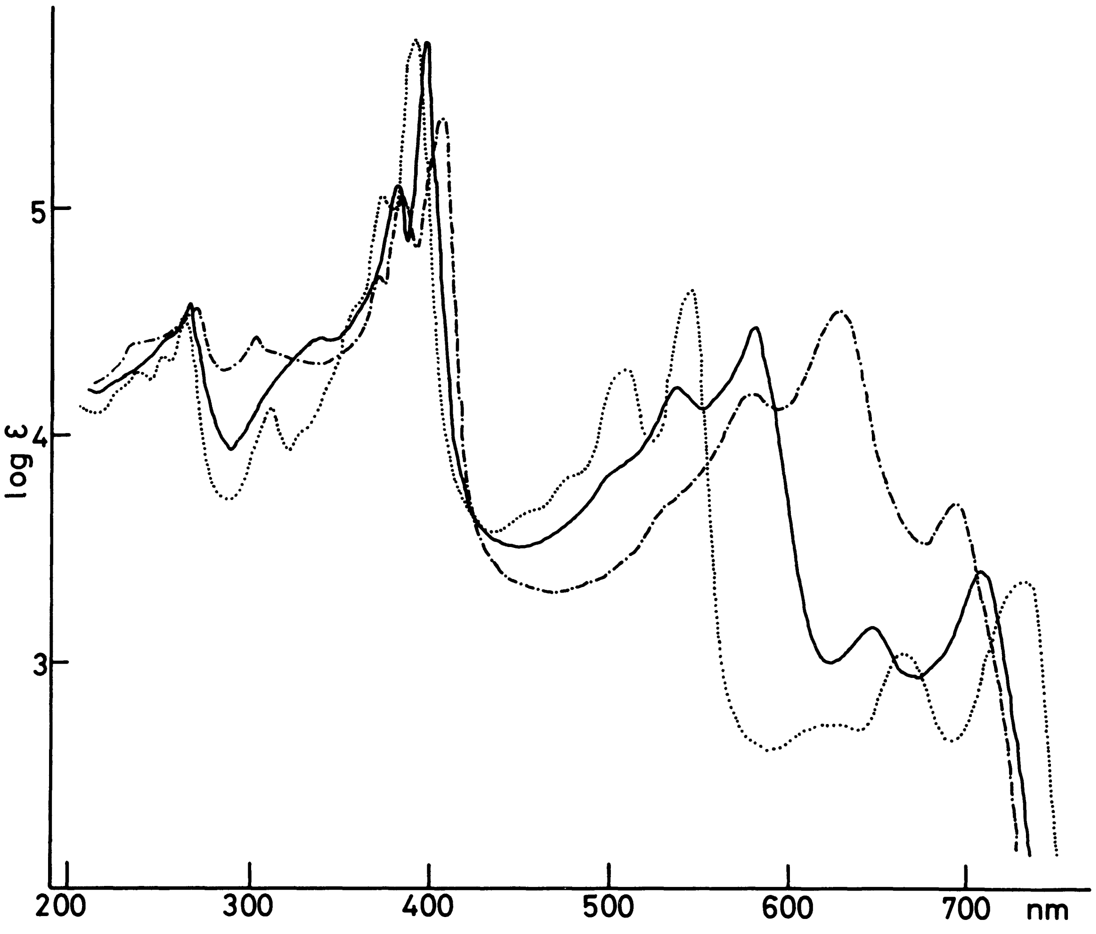
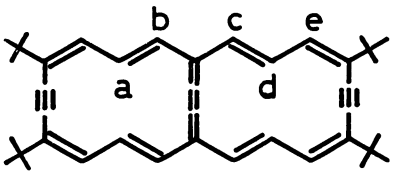
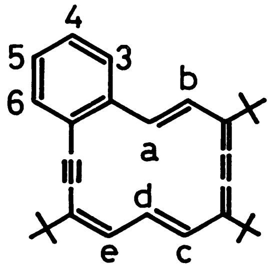


Fig. Electronic spectra of I (—·—·—), II (———) and V (·······) in THF.

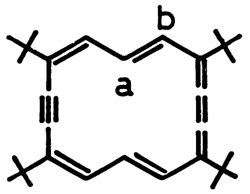
analogue (II), because the peripheral conjugated system ($I_c \leftrightarrow I_b$) has two equivalent Kekulé structures containing an *o*-quinoid and a benzenoid systems just as the case of the dinaphthobisdehydro[14]annulene (III). However, in fact, no appreciable intensification of diatropicity of I could be observed as compared with that of II. The $^{1}$H NMR spectrum of I suggests that the annulenoannulene (I) consists of two benzobisdehydro[14]annulene (VI) moieties, because the low-field shift of signals of all protons in I as compared with those of VI can be regarded as a result of deshielding effect of ring current induced in each ring. The high-field shift of outer H$^{e}$ signal in I as compared with that of H$^{c}$ can be attributed to a decrease of deshielding effect of the neighbouring ring along with the increase of distance from the ring. Unusual low-field shifts of H$^{3}$ and H$^{b}$ in I can be ascribed to an additive effect of steric compression and ring current.



V



VI

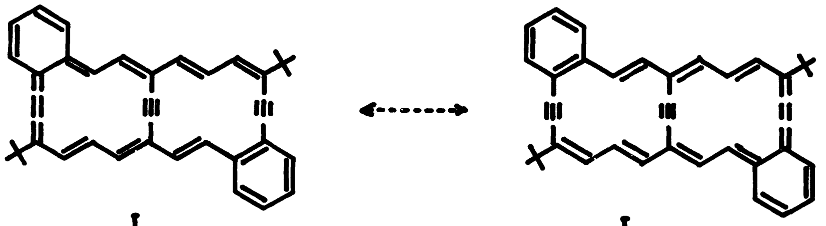


VII

Table. 100 MHz $^{1}$H NMR Parameters. τ-Values (J in Hz)

| | I | II | VI | VII | V |
|---|---|---|---|---|---|
| a | 8.70d(15.5) | 7.13d(15.5) | 9.19d(15.5) | 14.39t(13.5) | }12.85dd<br>(13,14) |
| d | 8.75dd<br>(14.5,12.5) | 7.15dd<br>(14.5,12) | 9.29dd<br>(14.5,12) | | |
| g | | }13.72t(13.5) | | | |
| j | | | | | |
| b | 0.57d(15.5) | 0.50d(15.5) | 1.03d(15.5) | 0.58d(13.5) | }-0.16d<br>(14) |
| c | 1.05(14.5) | 1.08d(14.5) | 1.70d(14.5) | | |
| e | 1.41(12.5) | 1.63d(12) | 1.67d(12) | | 0.39d<br>(13) |
| f | | 0.16d(13.5) | | | |
| h | | 0.43d(13.5) | | | |
| i | | 0.26d(13.5) | | | |
| k | | 0.45d(13.5) | | | |
| 3 | 0.81m | 0.92m | 0.98m | | |
| 4,5 | 2.08m | 2.18m | 2.26m | | |
| 6 | 1.31m | 1.42m | 1.48m | | |
| *t*-Bu | 8.19s | 8.02s, 8.25s | 8.30s, 8.32s,<br>8.36s | 8.10s | 7.99s |
| | $CDCl_3$-$CS_2$<br>31°C | $CDCl_3$<br>32°C | THF-$d_8$<br>35°C | THF-$d_8$<br>35°C | $CDCl_3$<br>35°C |

The $^{1}$H NMR parameters of II clearly indicate the induction of independent ring current with different intensities in both rings being stronger in the non-annelated 14π-system as evidenced by the much higher field signals of inner protons ($H^{g}$ and $H^{j}$). The $^{13}$C chemical shifts of sp-hybridized carbon atoms ($C^{A}$ δ 95.5, $C^{B}$ 100.0, $C^{C}$ 105.3, $C^{D}$ 113.4 ppm with respect to TMS as an internal standard) suggest an increased acetylenic character of $C^{A}$-$C^{B}$ bond. Such a large difference between sp-hybridized carbon atoms could not be observed in the parent [14]annuleno[14]annulene (V).8) The $^{13}$C NMR spectrum of I seems to afford more confirmative evidence on the nature of annelated annulenoannulenes, but unfortunately the measurement could not be feasible owing to the poor solubility.



$I_b$ $I_c$

The $^{1}$H and $^{13}$C NMR characteristics seem to indicate a superior contribution of structure $I_a$, and the fact that the $^{1}$H parameters of benzannelated moiety of II show close similarity with those of I indicates the minor contribution of structures of $I_b$ and $I_c$. Consequently, the dibenzannelated annulenoannulene (I) can be regarded as a condensed system consisting of two 14π-electron systems being consistent with our view on non-annelated symmetrical annulenoannulenes such as the trisdehydro[14]annuleno[14]annulene (V)4) and analogous trisdehydro-9) and hexakisdehydro[18]annuleno[18]annulenes.10)

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