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SYNTHESIS AND SPECTRAL PROPERTIES OF TRIBENZO[c,i,o]TRIPHENYLENE AND ITS ANIONS.

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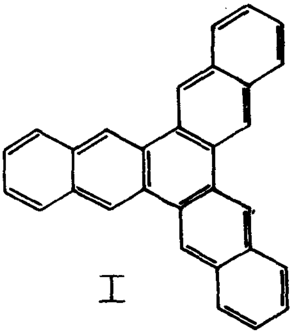
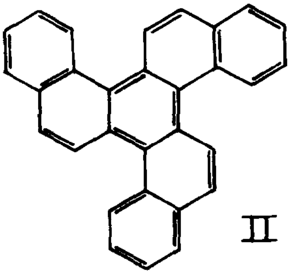
According to E.S.R. experiments on the mono- and di-negative ions of trinaphthylene (I) the electronic ground state of the mono anion of I is orbitally non-degenerate and the dianion is in a singlet ground state$^{1)}$. These results are in agreement with S.C.F. calculations of the anions of I, which show that the lowest antibonding level is non-degenerate in contrast with most other aromatic molecules and ions with trigonal symmetry.

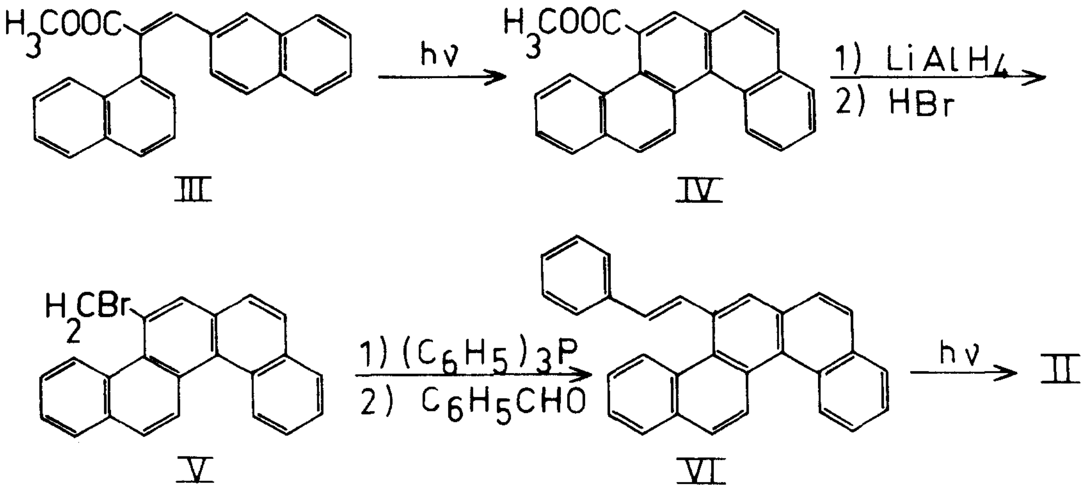

I


II

The same type of calculations on an isomeric molecule, tribenzo[c,i,o]triphenylene (II) showed that the lowest two antibonding orbitals are degenerate. One might expect therefore its dianion to have a triplet ground state.

Whereas trinaphthylene (I) and some other linear benzologues of triphenylene (starphenes)$^{2)}$ have been described, no synthesis is reported of the nonlinear isomer tribenzo[c,i,o]triphenylene (II). We prepared this compound according to the route given in the scheme.

The esterified product III of the Perkin condensation of α-naphtylacetic acid and β-naphtaldehyde was irradiated in benzene giving 13-carbomethoxy benzochrysene (IV) in 80% yield.



A Wittig synthesis with the triphenylphosphonium salt of V and benzaldehyde gave 13-styryl benzochrysene (VI) in 75% yield; mp 201-202.

Photodehydrocyclization of VI in benzene or hexane gave compound II; yield ca. 60%.

A second product (mp 197°) was isolated from the irradiation mixture and identified as 12-phenyl naphto[2-1, b]pyrene. Tribenzo[c,i,o]triphenylene forms pale yellow crystals melting at 233-234°C. Molecular weight: 378 (mass spectrum). Ultra violet spectrum see fig.1.

The NMR spectrum (fig.2) consists of three sets of absorptionlines with different chemical shifts and with equal integrated intensity. According to the classification of Martin3) these sets can be assigned to different types of protons; α-4 protons: H4 + H5; α+α/β protons: H1 + H6 and β protons: H2 + H3. The doublets of the AB system H5 - H6 are distinguishable from the underlying multiplets. The coupling constant $J_{5-6}=9,0$ cps is rather large for an aromatic system and points to a large double bond character of the bond C5 - C6. The calculated (Hückel) bond order C5 — C6 is .754 which is the largest one present in this molecule.

Contrary to our expectations, prolonged reduction of II with Na or K in 2-methyltetrahydrofuran yielded practically diamagnetic solutions. Moreover at 170°C, where the solvent forms a glass no triplet spectrum could be observed. Addition of II to these solutions restored the spectrum of the mono-negative ion with more than twice the maximum original intensity. The green colour of the dianion changed into the red colour of the mono-anion.

In addition to this the optical triplet spectrum of II has been measured in the temperature range from -170°C to -220°C (fig.3). This spectrum, which did not change with temperature, shows rather broad lines similar to the triplet spectra of ions with trigonal symmetry studied by van der Waals e.a.4). The explanation these authors presented may equally apply for our case. The spectrum may then be interpreted in terms of an assembly of molecules with different geometrical structure and consequently different zero-field splitting parameters X, Y and Z.

Taking the z axis perpendicular to the aromatic plane analysis of the spectrum shows that Z may vary from 0.0550 cm^{-1} to 0.0565 cm^{-1}, while the difference between X and Y varies from 0 to 0.030 cm^{-1}.

From the above experiments one may conclude that the dianion is in a singlet groundstate, in contradiction to expectations based on S.C.F. calculations. This discrepancy never observed before for similar trigonal aromatic systems[5)] may originate here from nonplanarity of II. Taking the system planar the distance between proton 4 and 5 is 0.6 Å only.
Steric factors, therefore, may lower the symmetry of the molecule and may be responsible for the singlet groundstate for the dianion and to different zero-field splittings X and Y for the optical triplet.

Fig.1 U.V. spectrum of tribenzo[c,i,o] triphenylene in methanol

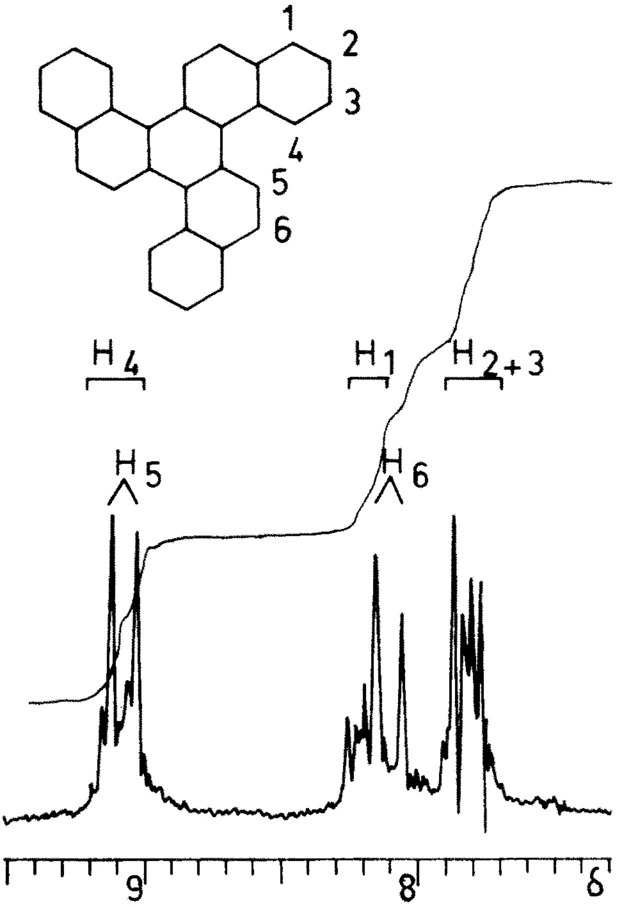


Fig.2 NMR spectrum of tribenzo[c,i,o] triphenylene in CS_2 (Varian HA100)

These deviations from planarity are not revealed by the N.M.R. spectrum; the peaks in the spectrum are quite sharp. This is not in contradiction with the E.S.R. results since the interconversion between various nonplanar structures may be rapid compared to the characteristic N.M.R. time scale, but slow with respect to the time scale in E.S.R.
From the maximum difference in X and Y observed the interconversion rates are estimated to be slower than 9.10^8 sec^{-1}.

We wish to thank Prof. E. de Boer for valuable discussions.

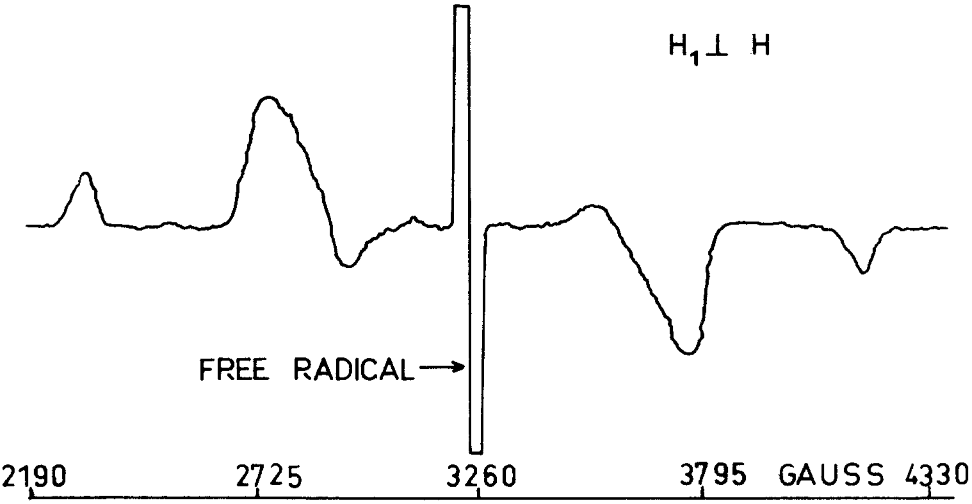


Fig.3 E.S.R. spectrum of the optical triplet of II. at -200°C in 2-methyl tetrahydrofuran.

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