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SYNTHESIS AND STRUCTURE OF *TRANS*-*TRANS*-TETRABENZO(*A*,*C*,*G*,*I*)CYCLODODECENE.

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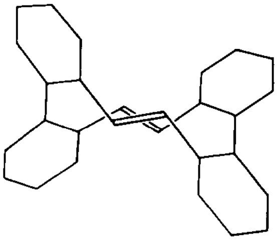
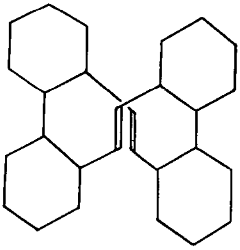
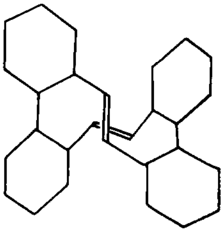
In 1955, Wittig *et al* reported as the first entry into the (12)annulene series, an elaborate synthesis of tetrabenzo(*a*,*c*,*g*,*i*)cyclododecene.[3] They obtained two geometrical isomers, to which the *cis*-*cis*- (mp 297.5-298^{0}) and the *trans*-*trans*-configuration (mp 163-164^{0}) were assigned. Very recently, the latter isomer was shown to be the 5-*cis* -15-*trans*-isomer.[4,5] A simple synthesis of the *cis*-*cis* and *trans*-*trans* isomers has been carried out by Sondheimer *et al*.[6] We wish to report a simple, one-step synthesis of an authentic 5-*trans*-15-*trans*-tetrabenzo(*a*,*c*,*g*,*i*)cyclododecene(I) applying a Wittig reaction. The structure of (I) has been established by X-ray crystallography.



I



II



III

A Wittig reaction between diphendialdehyde[7] and the bis-phosphorane derived from 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide[8] (lithium ethoxide) in dry dimethylformamide at 90° led to a mixture of products from which (I) was isolated in 3% yield.[9] The same product was obtained in dimethylsulfoxide(methylsulfinyl anion) at 23°. Substance (I) formed colourless crystals mp 312° (from benzene or ethylacetate). (*Anal*. *Found*: C,94.36; H,5.62. $C_{28}H_{20}$ requires: C, 94.34: H, 5.66). Mass Spectrum, molecular ion $M^{+\cdot}$ at m/e 356 (30%); M^{++} at m/e 178 (100%). IR (KBr) 3060, 3020, 2860(w), 1630(w), 1490, 1480(s), 1440(s), 1115, 945(s), 760(s), 645,620 and 570 cm^{-1}. UV max nm (log ε) (C_6H_{12}) 225(4.75) and 266(4.91); (CH_3CN) 224(4.48) and 267(4.45). NMR (100MHz, $CDCl_3$-$(CD_3)_2SO$) δ6.17(s,4H, vinyl) and 7.17-7.37 ppm (m, 16H, aromatic); in C_6D_6, the vinylic singlet was observed at 6.43 ppm. The physical properties of (I) indicate that it is a third geometrical isomer of tetrabenzo(*a*,*c*,*g*,*i*)cyclododecene, different from those described by Wittig.[3] Although the nmr chemical shift of the vinylic protons resembles that of *cis*-stilbene, the possibility of a *trans*-configuration was not excluded; a shielding effect by the benzene rings due to non-planar structure could account for the observed upfield shift of the vinylic absorption (relative to *trans*-stilbene). It is doubtful whether the absorption of the vinylic protons could be applied as a probe to establish whether (I) (as a (12)annulene) is paratropic.[10] The magnetic equivalence of the vinylic protons strongly favoured a *cis*-*cis*-, or a *trans*-*trans*-configuration. The former alternative was discarded on the basis of the infrared out-of-plane C-H bending vibration at 945 cm^{-1} (*trans*- CH=CH). The *trans*-*trans*-configuration of (I) was finally established by an X-ray crystallographic investigation.

Crystal Data: $C_{28}H_{20}$, F.W. = 356, m.p. = 312°, monoclinic, a = 16.810(5), b = 16.694(5), c = 13.835(4)Å, β = 98.41(2)°, U = 3840.6(8)Å^3, D_x = 1.23 g cm^{-3}, Z = 8. Absent spectra: ($hk\ell$) when $h + k = 2n + 1$, ($h0\ell$) when $\ell = 2n + 1$, space group *Cc* or *C2/c*, refined successfully in latter.

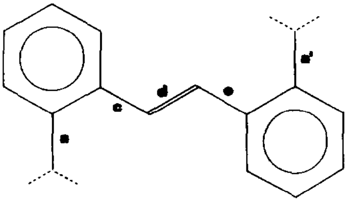
The cell dimensions and intensity data for 2416 independent observed reflexions with sin θ ≤ 0.896 were measured with a Picker 4-circle diffractometer (λ = 1.5418Å, monochromatised).

The structure was solved by multisolution weighted tangent-formula refinement using 596 reflexions with $|E| \geq 1.25$. Of 128 sign permutations only two had R_{alpha}[11] lower than 0.23. Both of these gave values of 0.22 for a point-atom E_{obs}/E_{calc} R factor based on the 28 highest *E*-map peaks while the corresponding values for other permutations ranged upwards from 0.45. The two solutions gave identical structures in which the asymmetric unit consisted of two half-molecules from which complete molecules were generated by the action of the crystallographic two-fold axis (Fig. 1). The twenty hydrogen atoms were among the 24 highest peaks of a difference map calculated after two cycles of isotropic refinement of the carbon skeleton (*R* = 0.12). Two further cycles of refinement, using individual isotropic temperature factors for the carbon atoms and a single variable overall isotropic temperature factor for the hydrogen atoms resulted in the current *R* factor of 0.089. Further refinement is in progress.

Theoretically there exist three alternative arrangements of the *trans*- double bonds in *trans*,*trans*-tetrabenzo(*a*,*c*,*g*,*i*)-cyclododocecene. Of these only (I) and (III) satisfy steric requirements for non-bonded interactions. In the present study we have found that the two independent molecules are both of type I. The finding that the crystal structure contains molecules bisected by two-fold axes in two directions at 90° to each other implies that the free molecule has $\underline{D}_2$(222) symmetry. This is reflected in the bond lengths which are equal within our experimental accuracy (σ = 0.005Å) for bonds which would be equivalent in this point-symmetry (Table I). There are slight differences in torsion angles, caused presumably by packing forces.

Table I. Bond Lengths in Å

	a	a'	c	e	d
Molecule I	1.481	–	1.465	1.472	1.332
Molecule II	1.504	1.483	1.465	1.474	1.337



The benzene rings are planar with bond lengths averaging 1.388 (r.m.s. 0.012) Å and internal valency angles averaging 120.0 (12)°. The mean C-H value is 1.05Å. No bond length or valency angle differs significantly from those reported for 5-*cis*-15-*trans* isomer implying that the two structures are equally strain free.

Although the title compound can be thought of as a (12)annulene derivative, the requirement of *trans*, *cis*, *cis*, *trans*, *cis*, *cis* conformations for the six double bonds of the annulene ring forces severe distortion from planarity and hence from aromaticity. The *trans* double bonds appear to be highly localized with bond lengths close to the value of 1.337Å given by Sutton[12]. Torsion angles around these bonds have values of 177.1° and 176.5°. The orientation of the phenyl rings is defined by the average values of the torsion angles at a and a' and at c and e which are 53(2)° and 130(2)° respectively.

Various geometrical isomers of (I) have recently been obtained by a different route.[5] One, of mp 301°, has been assigned the *trans*, *trans*- conformation. It is likely to be identical with (I) as an X-ray study[5] has shown that it also crystallizes in space group *C2/c* with eight molecules in the unit cell.

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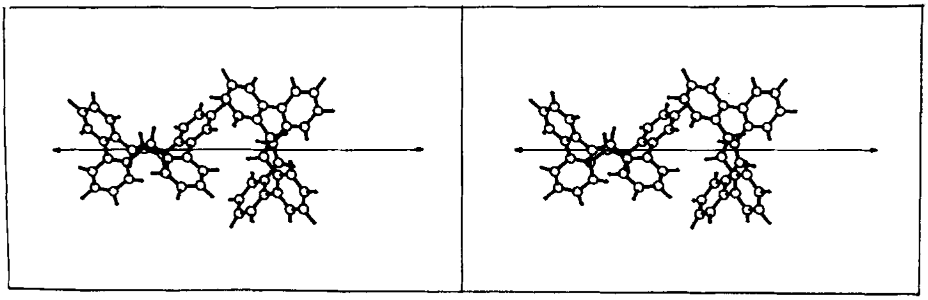

Figure 1