mixture was poured into a beaker and combined with 100 ml. of pentane. Water was then added dropwise with stirring until the lithium salts had congealed. The liquid was decanted through a filter and dried overnight over anhydrous sodium sulfate. Most of the solvent was removed with the aid of a rotatory evaporator. The n.m.r. spectrum of the residual crude III showed it to be contaminated slightly with the starting material IV and some other impurity, probably methylphenylacetylene.[8d] The product was diluted with 2 g. of pentane and chromatographed on 150 g. of acid-washed alumina (see the procedure for preparation of *trans*-IV). The first 50 ml. of product-bearing pentane eluate was collected. The solvent was removed on a steam-bath, and, after distillation through a 10-cm. Vigreux column, there was collected 5.0 g. (42%) of material of b.p. 82–85° (61–62 mm.) which consisted of 18% III, 54% *trans*-IIIa and 29% *cis*-IIIa.

***cis*-α-Methyl-β-deuteriostyrene** (*cis*-IIIa) was prepared from 82% *cis*-IV using the same procedure as for *trans*-IIIa except that the vinyllithium intermediate, which is distinguished by its intense red-brown color, was continuously treated with a 10% ether solution of deuterioacetic acid at a rate just sufficient to keep the solution colorless or slightly yellow throughout the reaction period of 50 min. This reaction was carried out on a 0.018-mole scale, and after chromatography of the product, the yield was 0.85 g. (39%). Analysis by n.m.r. spectrum indicated 36% III, 21% *trans*-IIIa, and 43% *cis*-IIIa with only minor impurities.

Hydroboration of *cis*- and *trans*-IV was carried out in diglyme (methyl ether of ethylene glycol) which had been distilled from sodium. Diborane was generated as required by dropwise addition of 10% solution of boron trifluoride in ether to a 10% solution of sodium borohydride in diglyme. A 5×10^{-3} *M* diglyme solution of a 60:40 *cis–trans* mixture of IV was placed in a 0.5 × 25-cm. thin-walled tube and diborane was bubbled through the solution for intervals of 10–60 sec., depending on the flow rate. After each interval, the *cis–trans* ratio was determined by v.p.c. analysis at 185° on acid-washed silicone rubber on Chromosorb. The ratio reached 36:64 after about 60% reaction.

COMMUNICATIONS TO THE EDITOR

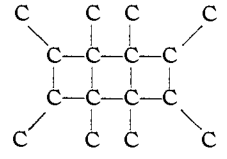
THE STRUCTURE OF A DIMER OF A DERIVATIVE OF CYCLOBUTADIENE

Sir:

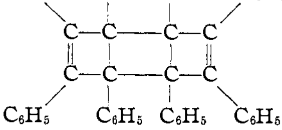
In 1960 Kitahara, Caserio, Scardiglia and Roberts[1] described the preparation of a dimer of fluorotriphenylcyclobutadiene $(C_{22}H_{15}F)_2$, (I), which they obtained by the action of phenyllithium on 1,1 - difluoro -2,4 - dichloro - 3 - phenylcyclobutene. Although dipole moment measurements, Raman spectra and nuclear magnetic resonance studies have since suggested that the substance might be *anti* - 1,2 - difluoro - 3,4,5,6,7,8 - hexaphenyl - tricyclo[4.2.0.0^{2,5}]octa-3,7-diene, other structures have not been ruled out absolutely. We are now completing an X-ray diffraction study of their material and can definitely confirm the stated structure.

The crystals are colorless triclinic blocks and the primitive unit cell contains two molecules of I (ρ calculated, 1.246 g./cc.; measured, 1.254 g./cc.). There are thus at least 3 × 46 = 138 positional parameters to be fixed to establish the positions of the carbon and fluorine atoms alone. This appears to be appreciably larger than any asymmetric unit previously solved without benefit of either heavy atom or isomorphous replacement methods and we did not at first expect to be able to derive a structure, particularly since the molecular skeleton was unknown.

Approximately four thousand nonequivalent X-ray reflections were measured with CuKα rays and statistical studies of these indicated the space-group to be P$\bar{1}$. A three dimensional sharpened Patterson function showed one particularly large, sharp peak which was the right size for the interactions between about sixteen atoms containing a pseudo-center of symmetry and the sixteen atoms related to them by the space-group's center of symmetry. With this indication of the location of the "center" of the molecule, a superposition of the Patterson was made with the translation equal to the distance between molecular "centers," and a minimum function was plotted. This eliminates, except for accidental coincidences, all interactions involving atoms not related to another by the pseudo-center in the molecule. The resulting diagram showed approximately the symmetry 2/m for a region about the origin and it was possible to account for the peaks with the *trans*-3-ring skeleton shown (with the proviso that two of the outer C's actually represent fluorine atoms).



With this start it was possible by difference maps and low resolution Fourier maps, in three steps, to locate the missing portions of the benzene rings and to show also which atoms are fluorines. Subsequent refinement has reduced the disagreement factor to 16% and the dimensions of the molecule and all intermolecular distances are reasonable, within present standard deviations, which are about ±0.03 Å. for a bond length. There can thus be no doubt of the correctness of the structure. The bond lengths indicate this basic bond structure



The central C_8 skeleton has very closely the summary 2/m. The angles between the plane of the cyclobutane ring and the planes of the cyclo-

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[1] Y. Kitahara, M. C. Caserio, F. Scardiglia and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).

butene rings are about 112 ± 2° with a *trans* configuration about the cyclobutane ring. The fluorine atoms are, of course, also *trans* with regard to the same ring.

Refinement continues and, when complete, full crystallographic details and data will be published elsewhere. We are indebted to Professor John D. Roberts for calling the problem to our attention and to Dr. Marjorie Caserio for providing the crystalline samples.

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RECEIVED MARCH 26, 1962

IDENTIFICATION OF A NEW TYPE OF MOLECULAR ASYMMETRY[1]

Sir:

Proton magnetic resonance has been used to show the non-equivalence of the two protons in a methylene group next to an asymmetric carbon atom.[2] Another type of molecular asymmetry has been found by this same technique. During an investigation of the oxidation of 2,6-di-*t*-butyl-4-methylphenol the stilbenequinone shown in Fig. 1 was prepared and its proton resonance spectrum obtained. The peaks derive from the *t*-butyl group and the aromatic protons were found to be doublets, with a further spin coupling between the non-equivalent aromatic protons. These results may only be explained by a non-equivalence of the substituents on either side of the central axis of the aromatic rings. If rotation about the central carbon–carbon bond were strongly hindered or if the conformation shown were energetically the most favorable, it is obvious that one side of a given aromatic ring is closer to the second aromatic ring than is the other side. However, even with rapid rotation, the two sides are non-equivalent in the *cis* as well as the *trans* conformation and the non-equivalence is not averaged by the rotation. The observed difference in magnetic environment is therefore quite reasonable. It is 0.03 p.p.m. for the *t*-butyl group and 0.54 p.p.m. for the aromatic protons, which are considerably closer to the site of the non-equivalence. A similar result was obtained starting with the appropriate *t*-amyl phenol. In this case separate peaks could not be observed for the non-equivalent ethyl part of the *t*-amyl group but the lines were significantly broadened. For the methyl groups in the *t*-amyl radical the separation was 0.04 p.p.m. and for the aromatic protons 0.51 p.p.m. A variety of similar molecules were

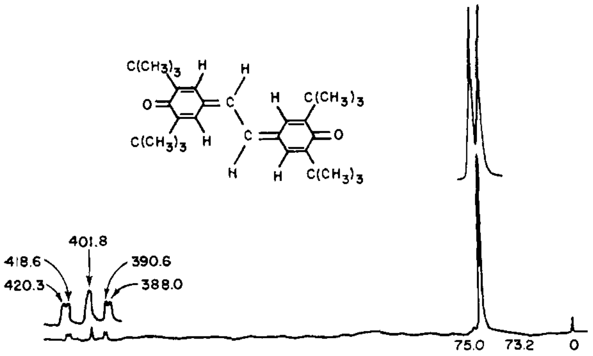
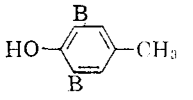
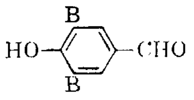
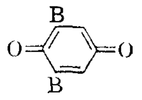
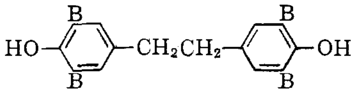
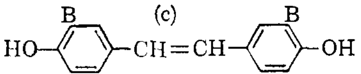


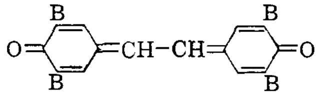
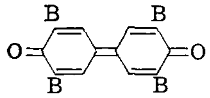
Fig. 1.—Proton resonance spectrum of stilbenequinone: peak positions are in cycles per second to low field of tetramethylsilane.

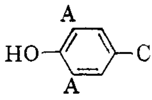
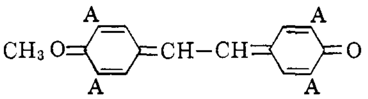
TABLE I

CHEMICAL SHIFTS OF SUBSTITUTED PHENOLS AND QUINONES[a]

			
$C(CH_3)_3$	1.49	1.50	1.31
CH_3	2.23	...	...
CH_2	...	...	...
Olefin CH	...	...	...
Aromatic CH	6.94	7.66	6.41
OH	4.77	5.78	...
CHO	...	9.79	...

		(c) 
$C(CH_3)_3$	1.36	1.50
CH_3	...	...
CH_2	2.74	...
Olefin CH	...	6.79
Aromatic CH	6.80	7.26
OH	4.70	4.97
CHO	...	...

			
$C(CH_3)_3$	1.30	1.33	1.36
CH_3	...		...
CH_2	...		...
Olefin CH	7.12		...
Aromatic CH	6.90	7.44	7.69
	J = 2.3 cycles		...
OH	...		...
CHO	...		...

			
$C(CH_3)_3$	1.34	1.27	1.30
	Ethyl CH_3 = 0.63	Ethyl CH_3 = 0.64	
	Ethyl CH_2 = 1.84	Ethyl CH_2 = 1.81	
	J = 7.1 cycles	J = 7.3 cycles	
CH_3	2.22	...	
CH_2	...	...	
Olefin CH	...	7.14	
Aromatic CH	6.76	6.92	7.42
OH	4.75	...	
CHO	...	...	

[a] Listed in parts per million to low field of tetramethylsilane. [b] B represents the *tert*-butyl group and A the *tert*-amyl group. [c] This is assumed to be the *trans* isomer but the configuration is not proven.

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[1] Published as N.R.C. No. 6860.

[2] P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).