addition, the spectra indicated that all contained the same number of methyl groups, but that (III) contained an extra ethyl group. It remains to be determined whether the C_5 substituent is methyl and the C_6 substituent is ethyl or *vice versa*.

The authors wish to thank Drs. S. F. MacDonald and H. J. Bernstein of the Division of Pure Chemistry for generous assistance. Analyses were carried out by Mr. A. E. Castagne.

(17) N. R. C. Postdoctoral Fellow, 1959–1961.

(18) N. R. C. Postdoctoral Fellow, 1960–1961.

(19) N. R. C. Postdoctoral Fellow, 1961–1962.

DIVISION OF APPLIED BIOLOGY
NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA
A. S. HOLT
D. W. HUGHES[17]
H. J. KENDE[18]
J. W. PURDIE[19]

RECEIVED MAY 4, 1962

CONFORMATIONAL ANALYSIS. XXXI. THE ISOPROPYL GROUP[1,2,3]

Sir:

Conformational energies of simple alkyl groups are the fundamental quantities on which conformational analysis is based, and values for the methyl and ethyl groups are known[4] to be about 1.8 kcal./mole. The numerical values previously reported for the isopropyl group range from 2.5 to 3.55 kcal./mole,[5–7] with the value 3.3 being commonly quoted.[4a] Other evidence[8] has been taken as support for a value for isopropyl which is considerably greater than those of methyl and ethyl. A rough statistical treatment of the problem suggests that while the axial isopropyl loses rotational freedom to a greater extent than do the smaller groups, the effect is small, and partially cancelled by an opposing enthalpy difference, and it can be predicted that at ordinary temperatures the free energy of an axial isopropyl should be only slightly greater than those of methyl and ethyl. If this prediction were to be correct, it would mean that the *a priori* assumption often made that an isopropyl group is almost as "big" as a *t*-butyl group[9] and is sufficient to establish a fair degree of conformational homogeneity in simple molecules would have to be abandoned, except as a rough approximation.

The free energy of an axial isopropyl (relative to an equatorial) has therefore been determined in two independent ways. First, 1,3-diisopropylcyclohexane has been equilibrated at elevated temperatures with a palladium catalyst,[10] the composition of the equilibrium mixture was determined by gas phase chromatography on a column of γ-methyl-γ-nitropimelonitrile, and the ΔF^0 for the isomerization[11] *trans* ⇄ *cis*-1,3-diisopropylcyclohexane was found to be -1.91 ± 0.01 kcal./mole at 560°K. When the symmetry properties of the molecule are taken into account, from this value one calculates that for the reaction *equatorial* isopropyl ⇄ *axial* isopropyl, $\Delta F^0_{298} = 2.10$ kcal./mole.

An independent measurement of the free energy of an axial isopropyl group was also made by determining the equilibrium point for the isomerization of the *cis* and *trans* ethyl 4-isopropylcyclohexanecarboxylates. The free energy of an axial ethyl carboxylate group was determined in the present work (by equilibration of the ethyl 4-*t*-butylcyclohexanecarboxylates) as 1.24 kcal./mole at 373°K., in agreement with literature values.[12] One can then calculate the free energy of the alkyl group from the measured equilibrium constant using the equation $\Delta F^0_{\text{alkyl}} = RT \ln [(K_iK_{\text{COOEt}} - 1)/(K_{\text{COOEt}} - K_i)]$, where K_i is the observed constant for the *cis* ⇄ *trans*-isomerization and K_{COOEt} is the constant for an axial ⇄ equatorial carbethoxyl.

In this work the equilibration was carried out at temperatures in the range of 329–416°K. using ethanol as solvent with sodium ethoxide catalyst. The analysis was done by gas chromatography on a Tide column, and the observed equilibrium constants gave $\Delta F^0 = 2.49$ (at 416°) and 2.22 (at 329°), which gives a value of $\Delta F^0 = 2.12$ kcal./mole at 298°. Similar studies were carried out with the 4-methyl and 4-ethyl carboxylates and the data are summarized in Table I. These values lead to standard free energy changes as given in Table II.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REACTION ETHYL *cis*-4-ALKYLCYCLOHEXANECARBOXYLATE ⇄ ETHYL *trans*-4-ALKYLCYCLOHEXANECARBOXYLATE

T, °K.	Me	Et	*i*-Pr	T, °K.	*t*-Bu
416.2	3.30	3.33	3.78	415.7	4.61
375.1	3.97	4.01	4.44	376.7	5.26
352.9	4.34	4.26	4.85	352.4	5.83
329.1	4.90	4.77	5.38	329.4	6.55

TABLE II

VALUES[a] FOR THERMODYNAMIC QUANTITIES FOR THE REACTION EQUATORIAL ⇄ AXIAL ALKYLCYCLOHEXANE AT 298°K.

Alkyl	ΔF^0, kcal./mole
Methyl	1.87
Ethyl	1.80
Isopropyl	2.11

[a] Calculated from the experimental data in Table I. The probable error in ΔF^0 estimated to be 0.1 kcal./mole.

The qualitative conclusion is that the isopropyl group is essentially the same size (in the present

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(1) Paper XXX, N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, in press (1962).

(2) This research was supported by a grant from the National Science Foundation.

(3) The new compounds used in this work were all obtained by straight forward unequivocal methods and gave proper analytical data.

(4) (a) W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, 1956, p. 1; (b) N. L. Allinger and S. Hu, *J. Am. Chem. Soc.*, **84**, 370 (1962).

(5) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(6) D. S. Noyce and L. J. Dolby, *J. Org. Chem.*, **26**, 3619 (1961).

(7) H. van Bekkum, P. E. Verkade and B. M. Wepster, *Konikl. Ned. Akad. Wetenschap. Proc. Ser. B*, *64*, No. 1, 161 (1961).

(8) (a) A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956); (b) W. Tagaki and T. Mitsui, *J. Org. Chem.*, **25**, 1476 (1960).

(9) For example, (a) W. Klyne, *Experientia*, **12**, 119 (1956); (b) B. C. Lawes, *J. Am. Chem. Soc.*, **84**, 239 (1962).

(10) N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959); **82**, 2553 (1960).

(11) Values for ΔH^0 and ΔS^0 were obtained but are anomalous, presumably because of the presence of appreciable amounts of boat forms at the high temperatures used. Further discussion will be given in the full paper.

(12) (a) E. L. Eliel, H. Haubenstock and R. V. Acharya, *J. Am. Chem. Soc.*, **83**, 2351 (1961); (b) N. L. Allinger and R. J. Curby, *J. Org. Chem.*, **26**, 933 (1961); (c) E. L. Eliel and M. Gianni, *Tetrahedron Letters*, 97 (1962).

sense) as a methyl or ethyl group, and in quite a separate class from the *t*-butyl group.

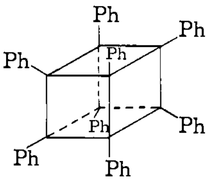
DEPARTMENT OF CHEMISTRY NORMAN L. ALLINGER
WAYNE STATE UNIVERSITY LESLIE A. FREIBERG
DETROIT 2, MICHIGAN SHIH-EN HU

RECEIVED APRIL 19, 1962

TETRAPHENYLCYCLOBUTADIENE DERIVATIVES. IV.[1] "OCTAPHENYLCUBANE"; A DIMER OF TETRAPHENYLCYCLOBUTADIENE

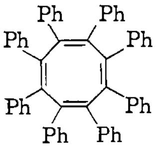
Sir:

We wish to report compelling evidence that the previously reported[2] tetraphenylcyclobutadiene dimer of m.p. 430° is "octaphenylcubane" (I), the first organic compound to incorporate eight carbon atoms bonded to each other symmetrically in the shape of a cube.

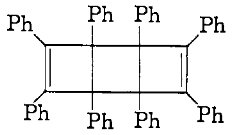


I

Dimerization of the radical intermediate from the thermal decomposition of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)-dimethyltin bromide leads to I in 85% yield.[2] Its non-identity with hexaphenylbenzene, from which it cannot be distinguished on the basis of analysis or melting point, was established by comparison with an authentic sample prepared by the method of Dilthey.[3] By analogy with the dimerization products of substituted cyclobutadienes obtained by previous workers,[4] the most likely structure for our dimer might be octaphenylcycloöctatetraene[5a] (II) or the octaphenyltricycloöctadiene, III.[5b] However,



II



III

the saturated character of the dimer is unequivocally established by its solid-state Raman spectrum[6] which exhibits a strong phenyl band at 1605 cm.$^{-1}$ (also present in the solid state infrared spectrum at 1603 cm.$^{-1}$) but contains no band reasonably assignable to a double bond stretching mode. In contrast, other unsaturated compounds in this series exhibit a very strong Raman band in the vicinity of 1625–50 cm.$^{-1}$ (see below) and the absence of such a band effectively eliminates II and III as potential candidates.[5] This confirms our previous conclusions, based on preliminary X-ray symmetry considerations.[7]

Further X-ray diffraction experiments on the needle-like single crystals of I have shown the lattice to be body-centered tetragonal, with space group C_{4h}^6–$I4_1/a$, established without ambiguity. Cell constants were derived from single-crystal and from powder data: $a = 19.489 \pm 0.019$ Å.; $c = 10.647 \pm 0.011$ Å. The morphological needle axis is [001]; the only developed faces are [100]. The measured density, by flotation and by displacement, is 1.173 ± 0.008 g. cm.$^{-3}$; the density calculated on the basis of four molecules of $(C_7H_5)_8$ per cell is 1.171 g. cm.$^{-3}$. Reasonably complete three-dimensional diffracted-intensity data have been gathered about both [100] and [001] with the Weissenberg technique, and a full structure determination is in progress by D.R.P. Arguments based upon the X-ray evidence indicate that discrete molecules of formula $C_{56}H_{40}$ exist in the crystalline state, and that each such molecule is at a position of $\bar{4}$ symmetry within the cell. Though the present state of the X-ray investigation does not unequivocally establish the structure of the dimer as I, none of the data is in contradiction to this structure and, in the absence of an equally satisfactory alternative structure, the total body of chemical and physical evidence appears quite compelling.

The extreme insolubility of this dimer precluded normal chemical studies; reasonable solubility was obtained only in refluxing diphenyl ether, solutions of which yield well-formed crystals on cooling and from which its molecular weight was established ebulliometrically[8] in agreement with the X-ray result above. Exposure to hot concentrated sulfuric acid leads to a violet solution which yields a water-soluble ring-sulfonated mixture, and warming with concentrated nitric acid leads to indiscriminate nitration and an intractable mixture of products.

In an attempt to prepare the possible precursors, II and III, of the cubane I, it was found that two unrelated reactions unexpectedly yielded the same new product. Thus, while the reaction of equivalent quantities of 1,4-dilithio-*cis,cis*-tetraphenylbutadiene and 1,4-diiodo-*cis,cis*-tetraphenylbutadiene (route (1)) is expected to produce the D_{2h} ("tub") form of octaphenylcycloöctatetraene (IIa) and the treatment of 3,4-dibromotetraphenylcyclobutene[9] with phenyllithium in ether[10] (route

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[1] Part III, H. H. Freedman, *J. Org. Chem.*, in press.

[2] H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961).

[3] W. Dilthey and G. Hurtig, *Chem. Ber.*, **67**, 2004 (1934).

[4] (a) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957); (b) R. Criegee, *et al.*, *ibid.*, **93**, 1553 (1960); (c) M. Avram, *et al.*, *Tetrahedron Letters*, **1**, 21 (1961); (d) E. H. White and H. C. Dunathan, Abstracts of the 134th A.C.S. Meeting, Chicago, Ill., 1958, p. 41-P; (e) M. Avram, *et al.*, *Chem. Ber.*, **93**, 1789 (1960).

[5] (a) A recent publication (E. H. Braye, W. Hubel and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961)), reports the formation of a hydrocarbon $(C_{14}H_{10})x$ of m.p. 421° which appears to be identical with our dimer and, on the basis of its method of formation and ultraviolet spectrum, is assumed by the authors to be II. (b) Structure III has been assigned to the dimer by M. Tsutsui (*Chem. and Ind.*, 780 (1962).

[6] The authors are greatly indebted to Dr. John Evans for supplying the Raman data.

[7] Private communication by D. R. Petersen, cited by H. H. Freedman.[2]

[8] We are indebted to Dr. D. R. Stull for this determination and for the observation that the molecular weight tended to decrease with prolonged boiling in diphenyl ether. It is also of interest that the solution of I in this solvent is bright yellow and on cooling returns to its original colorless condition.

[9] H. H. Freedman and A. M. Frantz, Jr., paper presented before the Organic Division at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, Abstracts p. 26-O.

[10] The possibility that tetraphenylcyclobutadiene itself is an intermediate in this reaction is being currently investigated.