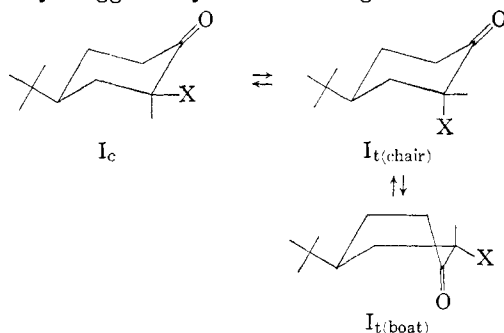


COMMUNICATIONS TO THE EDITOR

CONFORMATIONAL ANALYSIS. XVI. THE ENERGY OF THE BOAT FORM OF CYCLOHEXANONE. DIRECT MEASUREMENTS OF 2-ALKYL KETONE EFFECTS^{1,2}

Sir:

Klyne,³ in elaborating and extending earlier interpretations of Robins and Walker,⁴ suggested that the approximate eclipsing of the oxygen of a cyclohexanone by an adjacent equatorial group would destabilize the group in that position by approximately 1 kcal. relative to the axial conformation as compared to the analogous situation on the nicely staggered cyclohexane ring. What would be



a conformational equilibrium in a simple case can instead be studied as an isomerization by fixing the conformation of the ring by means of a *t*-butyl group in the 4 position.⁵ Such a *cis*-*trans* isomerization now has been studied for I with X = methyl, ethyl, isopropyl and *t*-butyl.

The synthesis of 2-methyl-4-*t*-butylcyclohexanone⁶ was carried out by Method A: the Friedel-Crafts reaction with *t*-butyl chloride and *o*-cresol, then hydrogenation to the cyclohexanol and Jones oxidation⁷ to the cyclohexanone. The same compound was obtained from 4-*t*-butylcyclohexanone by Method B: reaction with ethyl oxalate, decarbonylation, and methylation of the sodium salt of the resulting β -keto ester, followed by hydrolysis and decarboxylation. The compounds (I) with X = ethyl and isopropyl were prepared by Method B, and the compounds I with X = isopropyl and *t*-butyl were prepared by Method A.

Since Method A was expected to yield mainly the *cis* isomer,⁸ the isomer obtained in larger amount by this method was assigned the *cis* configuration.

(1) Paper XV, N. L. Allinger, H. M. Blatter, M. A. DaRooge and L. A. Freiberg, *J. Org. Chem.*, **26**, in press (1961).

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

(3) W. Klyne, *Experientia*, **12**, 119 (1956).

(4) P. A. Robins and J. Walker, *Chem. and Ind.*, 772 (1955); *J. Chem. Soc.*, 1789 (1955), 3960 (1954).

(5) See for example, N. L. Allinger, J. Allinger, L. A. Freiberg, R. Czaja and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960), and references therein.

(6) All new compounds were characterized by correct carbon and hydrogen analyses. The ketones were characterized in each case by their dinitrophenylhydrazone derivatives.

(7) R. G. Curtis, I. Hellbron, E. R. H. Jones and G. F. Woods, *J. Chem. Soc.*, 457 (1953).

(8) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1956, p. 190.

The mixture of isomers obtained was analyzed by vapor phase chromatography on a column made from the tricyanoethylation product of glycerol on firebrick. The mixture of isomers obtained from the synthesis was equilibrated with a basic alcoholic solution at two different temperatures, and the thermodynamic constants for the reaction were found in the usual way.⁹ The results are summarized in Table I. The ΔH for moving an alkyl group from an equatorial to an axial position is seen to go from 1.6 kcal./mole. for a methyl down to only 0.4 kcal./mole. for an *i*-propyl.

TABLE I
EQUILIBRATION DATA FOR THE REACTION *trans* \rightleftharpoons *cis*-2-
ALKYL-4-*t*-BUTYLCYCLOHEXANONE

X =	<i>t</i> , °C.	<i>cis</i> , %	ΔH	ΔS
Me	64.0	90.84	-1.57 ± 0.21	-0.1 ± 0.6
	25.0	93.08		
Et	64.6	82.17	-1.06^a	0^b
	25.0	86.37		
<i>i</i> -Pr	64.0	71.25	-0.44 ± 0.12	$+0.5 \pm 0.3$
	25.0	72.96		
<i>t</i> -Bu	90.3	89.45	-2.39 ± 0.38	-2.5 ± 1.0
	25.0	94.13		

^a Calculated assuming $\Delta S = 0$ (See *b*). ^b The vapor phase chromatographic curves were not completely separated, and there was some arbitrariness in the way the band resolution was carried out. The resolution was done in such a way as to make ΔS come out equal to zero (the expected value). ^c That little (X = Et) or no isomerization occurs on the vapor phase chromatographic column is shown by the clean separability of the isomers.

Fieser and Fieser¹⁰ have pointed out that in an equatorial 2-methylcyclohexanone the methyl group and oxygen atom are too far apart for any van der Waals repulsion to occur, and therefore no 2-alkyl ketone effect as envisioned by Klyne should be expected. Actually since a 2-axial methyl is further separated from the 6-axial hydrogen in a cyclohexanone than it is in the corresponding cyclohexane, shift of the equilibrium to give more of the axial form in the ketone than in the hydrocarbon might be expected. Experimentally (for the 2-methyl group) the shift is negligible. This may arise from a corresponding energy increase brought about by some other change, for example, bond angle distortions, but at any rate it seems clear that the ΔH for the equilibrium $I_a \rightleftharpoons I_e$ is essentially the same in the ketone as it is in the hydrocarbon.

In the ethyl and isopropyl compounds (I) models show that an interaction between a hydrogen of the methyl group (when the alkyl is axial) with the equatorial ring hydrogen on the next carbon can be eliminated when the adjacent methylene is replaced by a carbonyl group. No similar change is possible when the alkyl is equatorial. It can therefore be predicted that while the energy of the 2-axial methyl

(9) N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959).

(10) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 213.

is 1.6 kcal., the corresponding ethyl and isopropyl groups should have this energy reduced to 0.8 kcal./mole. Qualitatively it is seen that these groups do have smaller energies when axial than does the methyl, but the agreement is not quantitative. Djerassi¹¹ suggested from a consideration of the rotatory dispersion curves of menthone and isomenthone that the energy of an axial isopropyl adjacent to a carbonyl was less than that of an axial methyl β to a carbonyl (0.9 kcal.), and the present work bears out that suggestion.

The *t*-butyl case needs to be considered separately from the above since the values for ΔH and ΔS set it apart from the other groups. The enthalpy change of I (X = *t*-Bu) from the *cis* to the *trans* chair would be expected to be essentially the same as that found in the hydrocarbon (5.9 kcal./mole).¹² On the other hand, the enthalpy required to put a cyclohexanone ring in the boat form has been calculated¹³ to be only 2.7 kcal./mole. It therefore was predicted that *I_t* would exist in the boat form, and ΔH is in good agreement with this prediction. It has also been predicted that the boat form of cyclohexane would have a higher entropy than would the chair form.¹⁴ In the only case where this prediction was tested experimentally,¹² it was found to be true. The greater entropy of the *I_t* form (relative to *I_c*) when X = *t*-butyl is therefore expected and found.

(11) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 106, 187.

(12) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **82**, 2393 (1960).

(13) N. L. Allinger, *ibid.*, **81**, 5727 (1959).

(14) P. Hazebroek and L. J. Oosterhoff, *Discussions Faraday Soc.*, **10**, 87 (1951).

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CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPOUND OF TRIETHYLPHOSPHINE AND CARBON DISULFIDE¹

Sir:

Red monoclinic prismatic crystals are formed when triethylphosphine reacts with carbon disulfide in benzene or other solvents.² Analogous compounds are known for several other tertiary phosphines. The conflicting proposals for the molecular structures of these substances are reviewed by Issleib and Brack,³ who concluded incorrectly that they are loose molecular compounds. We have determined the structure of the triethyl compound by X-ray diffraction and find that there is a chemical bond between phosphorus and the carbon atom of CS₂. The shape of the molecule corresponds to a zwitterion of a quaternary phosphonium derivative of dithioformate as proposed by Jensen,⁴ (CH₃CH₂)₃P⁺—CSS⁻.

Single-crystal diffraction patterns were recorded with Cu K α radiation by Weissenberg and preces-

(1) This work was done under the auspices of the U. S. Atomic Energy Commission.

(2) A. W. Hofmann, *Ann. Suppl.*, **1**, 1 (1861).

(3) K. Issleib and A. Brack, *Z. anorg. u. allgem. Chem.*, **277**, 271 (1954).

(4) K. A. Jensen, *J. prakt. Chem.*, **148**, 101 (1937).

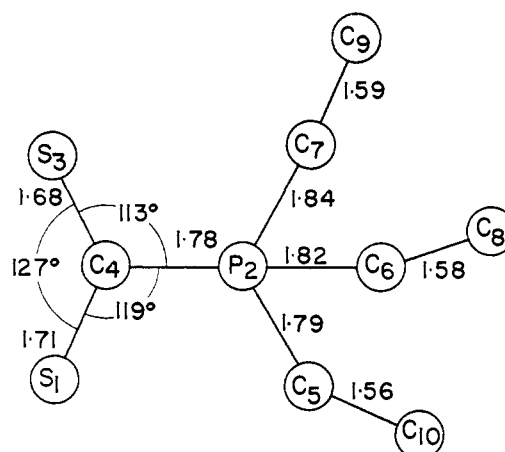


Fig. 1.—Bond distances in Å. and bond angles (not to scale).

sion techniques. The crystals are monoclinic, space group P2₁/c, with 4 molecules in the unit cell of dimensions:

$$\begin{aligned} a &= 7.50 \pm 0.02 \text{ \AA.} \\ b &= 11.97 \pm 0.02 \text{ \AA.} \\ c &= 13.82 \pm 0.05 \text{ \AA.} \end{aligned} \quad \beta = 123.1^\circ \pm 0.2^\circ$$

The density is calculated to be 1.24 g. cm.⁻³.

Atomic coordinates of P and S were found with the three-dimensional Patterson function. Electron density calculations revealed the carbon atoms and accomplished some refinement of the heavy-atom coordinates. Further refinement by full-matrix least squares with isotropic individual temperature parameters and 610 observed independent reflections reduced the conventional unreliability factor *R* to 0.11. The resulting atomic parameters are listed in Table I. Hydrogen atoms are omitted from these calculations. The phosphorus and sulfur atoms are not clearly distinguished by the X-ray data, but are identified on the basis that phosphorus is the atom bonded to the ethyl groups.

TABLE I

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å. ²
S ₁	0.127	0.114	0.141	6.3
P ₂	.132	.244	.329	4.4
S ₃	.089	.840	.401	5.7
C ₄	.056	.231	.183	5.4
C ₅	.104	.751	.169	5.1
C ₆	.300	.128	.416	5.6
C ₇	.279	.376	.392	5.9
C ₈	.348	.372	.042	6.3
C ₉	.479	.377	.380	6.7
C ₁₀	.249	.645	.218	7.8

The bond distances and some of the bond angles are shown in Fig. 1. Standard deviations are about 0.03 Å. for P—C and S—C bonds and 0.04 Å. for C—C bonds. The thioformate carbon (C₄) is coplanar with its three neighbors, and its bond angles ($\sigma = 1^\circ$) are typical of those of salts of carboxylic acids. The bond angles at the phosphorus atom range from 108° to 111° ($\sigma = 1^\circ$). The bond angles at the methylene carbon atoms (C₅, C₆, C₇) are 115°, 113°, and 109° ($\sigma = 2^\circ$).