A preliminary report of the space group of a copper dimethylglyoxime crystal has recently appeared (Bua & Schiavinato, 1951). The space group is reported to be $P2_1/n$ with four molecules in the unit cell. It would not be necessary, then, to have a centro-symmetrical molecule in the copper dimethylglyoxime structure.

The authors gratefully acknowledge the following aid which has made possible this and other structure determinations to be reported later: The Research Corporation for a Frederick Gardner Cottrell grant for purchase of instruments; Graduate School of Indiana University for a grant-in-aid to help punch master data used in structural calculations and the Office of Naval Research for extensive support under contract N onr-191 (00)-NR-052-245.

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The Molecular Structure of 1,1,2,2-Tetramethylcyclopropane*

By H. P. Lemaire† and R. L. Livingston

Department of Chemistry and Purdue Research Foundation, Purdue University, Lafayette, Indiana, U.S.A.

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The structure of 1,1,2,2-tetramethylcyclopropane has been investigated by electron diffraction. The results indicate an average C–C bond distance of 1·52 ± 0·03 Å and an external angle (CH_3–C–CH_3) of 114 ± 6°.

Introduction

The two main points of interest in connection with the structure of cyclopropane or of its derivatives are the C–C bond distance in the ring and the value of the external angle (the H–C–H angle in cyclopropane and the corresponding angle in its derivatives). There is evidence that the C–C distance is shorter than in most hydrocarbons and that the external angle is greater than tetrahedral. In cyclopropane Pauling & Brockway (1937) have given 1·53 ± 0·03 Å and 109·5° for these parameters; more recently Bastiansen & Hassel (1946) found values of 1·535 Å and 118·2 ± 2°. In 1,1-dichlorocyclopropane O'Gorman & Schomaker (1946) have found a C–C distance of 1·52 ± 0·02 Å and a Cl–C–Cl angle of 112 ± 4°. Smith (1941), from infra-red data, arrived at an exterior angle of 136° in cyclopropane, assuming a C–H bond distance of 1·09 Å and a C–C bond distance of 1·53 Å. However, it was later shown by Skinner (1947) that the moment of inertia determined by Smith is compatible with the model of Bastiensen & Hassel.

The results of this work indicate that in 1,1,2,2-tetramethylcyclopropane the average C–C bond distance is 1·52 ± 0·03 Å and the external angle (CH_3–C–CH_3) is 114 ± 6°.

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* From the Ph.D. Thesis of H. P. Lemaire, Research Corporation Fellow in Chemistry, Purdue University, 1949–50.

† Present address: Department of Chemistry, St. Michael's College, Winooski Park, Vermont, U.S.A.

Experimental

The sample of the compound used in this investigation was provided by Dr Greenlee of Ohio State University. It has an estimated purity of at least 98% and the following physical constants: b. p. 75·89° C. (760 mm.); $n^{20}D$ 1·4009, d_4^{20} 0·7170; f. p. −81·05° C.; T_{f_0} (estimated by the 'midpoint' method) −80·82° C.

Electron-diffraction photographs were prepared in the customary manner (Brockway, 1936), using an apparatus built by Dr H. J. Yearian of the Purdue Physics Department. The camera distance was about 108 mm. and the electron wave-length about 0·055 Å. The recorded pattern extended to a q of about 94.

Interpretation

The radial distribution method (Pauling & Brockway, 1935; Shaffer, Schomaker & Pauling, 1946) and the visual correlation method (Brockway, 1936; Pauling & Brockway, 1934) were used in the interpretation of the recorded pattern. The radial distribution function was calculated from the equation

$$rD(r) = \sum_{q=1,2,\ldots}^{q\,\max} I(q)\exp(-bq^2)\sin\left(\frac{\pi}{10}qr\right)$$

by the use of punched cards (Shaffer *et al.*, 1946). The values of $I(q)$ were taken from the visual intensity curve (curve 'Vis', Fig. 2) which was drawn assuming no falling off of intensity with increasing q. The constant b was chosen so that $\exp(-bq^2) = 0{\cdot}10$ at $q = 100$.

The resulting curve (Fig. 2) shows two major peaks; the peak at 1·52 Å corresponds to the average C–C bond distance and the one at 2·62 Å to non-bonded C–C distances of the type C_4–C_5, C_4–C_1 and C_4–C_3 (Fig. 1).

The peak at 1·08 Å is in good agreement with the expected value for the C–H bond but it is not as reliable as the other two peaks. The vertical lines beneath the curve correspond to the interatomic distances in one of the best models ($L_{1\cdot54}$) as determined by the correlation method.

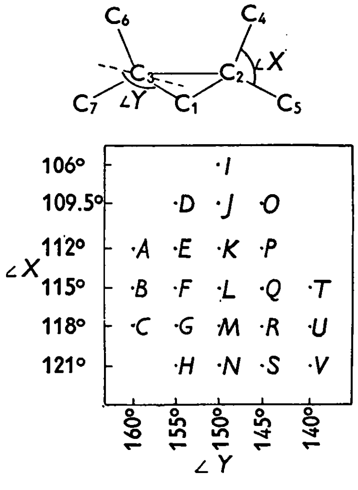

Fig. 1. Types of models constructed and parameter ranges studied.

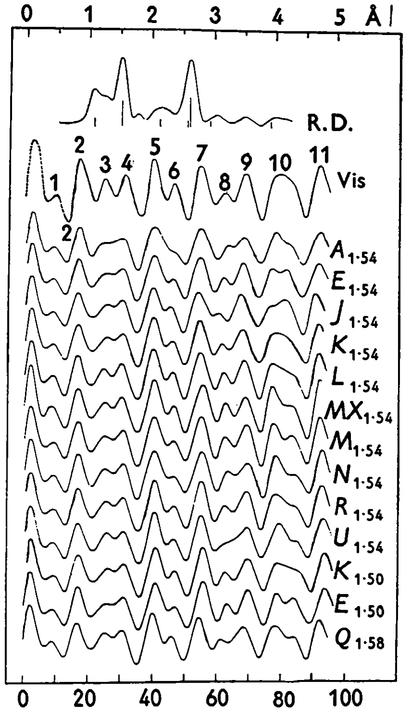

Fig. 2. Radial distribution function and intensity curves.

The theoretical intensity curves were calculated from the expression

$$I(q) = \sum_i\sum_j \frac{Z_iZ_j}{r_{ij}}\exp(-b_{ij}q^2)\sin\left(\frac{\pi}{10}qr_{ij}\right).$$

The constant b_{ij} in the exponential vibration factor was assigned the value 0·00018 for bonded C–H terms, 0·0003 for non-bonded C–H terms, and zero for all C–C terms. All H–H terms and all C–H distances which change upon rotation of the side-chain methyl groups were not included in the calculations.

A few simplifying assumptions were made to reduce the number of structural parameters. The C–H bond distances were taken to be 1·09 Å and the H–C–H angles were assumed to be 109·5°. The C–C bond distances in the ring were assumed equal and the side-chain carbon atoms were assumed to be symmetrically disposed so that the carbon skeleton has C_{2v} symmetry. The problem was thus reduced to one of four parameters, the following being chosen: (1) the C–C distance in the ring (C_1–C_2), (2) the C–CH_3 distance (C_2–C_4), (3) the external angle ($\angle X$) and (4) the angle, measured in the plane of the ring, between a plane drawn through the CH_3–C–CH_3 group and the C–C bond direction in the ring ($\angle Y$).

All models were calculated using a side-chain C–C distance of 1·54 Å. The external angle, X, was varied from 106° to 121° in 3° increments, and the angle Y

was varied from 160° to 140° (10° on either side of the most symmetrical—150°—arrangement in which the plane through the CH_3–C–CH_3 group bisects the angle of the ring) in 5° increments. Values of the ring C–C distance were chosen as 1·50, 1·54 and 1·58 Å. Models with ring C–C distances of 1·42, 1·46, 1·62 and 1·66 Å were also calculated but only for more restricted ranges of the angular parameters, since these appeared incompatible with the radial distribution curve.

The representative curves shown in Fig. 2 are lettered according to the parameter chart in Fig. 1; the subscript denotes the ring C–C distance used in calculating the model. The change in the pattern with changes of the angular parameters for models with C–C = 1·54 Å is representative of the change for other values of the ring C–C distance.

Curves for models $K_{1{\cdot}54}$, $L_{1{\cdot}54}$, $M_{1{\cdot}54}$, $Q_{1{\cdot}54}$ and $R_{1{\cdot}54}$ are in good agreement with the visual curve. Curves $E_{1{\cdot}54}$, $F_{1{\cdot}54}$ and $G_{1{\cdot}54}$ do not agree with the visual curve in that they show a doublet for the tenth maximum; these three curves were not rejected, however, owing largely to the fact that some allowance for vibration of the heavy atoms might well bring them into agreement. An attempt was made, in every case, to allow for such effects.

Models having an angle Y of 160° are illustrated by curve A; all were rejected on the basis of the appearance of the sixth and eighth maxima.

Curve J is not acceptable because of wrong relative depths of the eighth and ninth minima; models D and O gave rise to curves showing even poorer agreement with the visual curve.

Curve N, typical of curves with angle X greater than 118°, has the eighth minimum too deep relative to either the seventh or the ninth minima and was rejected on that basis.

Model U is not acceptable since the curve does not show a peak corresponding to the eighth maximum; this is characteristic of models with $\angle\ Y = 140°$.

Curve MX differs from curve M in that it was obtained from a completely rigid molecule with no vibration factors for any of the terms. The difference between the two curves illustrates the qualitative effect of excluding C–H terms which change upon rotation of the methyl groups and of placing vibration factors on the others; the quantitative effect is also very small.

Curves $K_{1{\cdot}50}$ and $Q_{1{\cdot}58}$ are typical of the best models obtained for the indicated ring C–C distances. The best models for ring C–C distances of 1·50 Å and 1·58 Å are in as good agreement with the visual curve as models with all C–C distances equal to 1·54 Å.

For a ring C–C distance of 1·50 Å, acceptable models were obtained for values of angle X from 109·5° to 118° and for values of Y from 155° to 145°. The best model is in the region of $K_{1{\cdot}50}$. The region of acceptability for C–C (ring) = 1·58 Å extends from $X =$ 112° to 118° with Y either 150° or 145°. The best model is in the region of $Q_{1{\cdot}58}$.

From these results it is concluded that the external angle (angle X) is 114±6° and angle Y is 150±8°. These values correspond to a C(ring)–C(ring)–CH_3 angle of approximately 118°.

Table 1. *Quantitative comparisons for model* $L_{1{\cdot}54}$

Maximum	Minimum	q_0	$q/q_0(L_{1{\cdot}54})$
	2	13·59	(0·934)
2		16·96	0·996
	3	22·15	0·952
3		25·18	0·997
	4	28·49	0·972
4		31·64	0·967
	5	36·67	0·974
5		40·68	1·003
	6	44·60	0·998
6		47·23	0·991
	7	51·30	0·980
7		55·57	0·999
	8	60·00	1·001
8		63·30	0·995
	9	65·95	0·993
9		70·09	0·990
	10	74·80	0·990
10		81·07	—
	11	89·06	1·000
11		94·00	0·992
		Mean	0·988
		Mean dev.	0·011

Quantitative comparisons for one of the best models are given in Table 1. A consideration of all the acceptable models shows that the range of ring C–C distances is greater than the range of side-chain C–C distances, and hence the latter is determined with more precision. The final bond distances are:

$$\text{C–C(ring)} = 1{\cdot}52+b\pm0{\cdot}04\ \text{Å}\ ,$$
$$\text{C–C (side-chain)} = 1{\cdot}52-b\ ,$$

where $-0{\cdot}04 \leq b \leq 0{\cdot}04$. The average C–C distance is more accurately determined as 1·52±0·03 Å. Comparison of the final distances in model $L_{1{\cdot}54}$ is made with the radial distribution curve in Fig. 2.

Discussion

The results obtained in this investigation are in fairly good agreement with the results of studies on other cyclopropane derivatives to which reference has been made in the introduction. The best value for the external angle (114°) found in this study is smaller than the value of 118·2° found by Bastiansen & Hassel (1946) in cyclopropane, although it is impossible to exclude tetramethylcyclopropane models having values of this angle as large as 120°. An external bond angle of 114° does not confirm values of 120° (Walsh, 1949) and 122° (Kilpatrick & Spitzer, 1946) proposed on the basis of bond-orbital theories. It agrees well, however, with the value of 113° calculated by Coulson & Moffitt (1947) who introduced somewhat different assumptions into the bond-orbital method.

The authors are very grateful to Dr H. J. Yearian for the use of his diffraction apparatus and his generous assistance in the experimental work. They also wish to thank Dr Greenlee, of Ohio State University, for the sample and the Research Corporation for the financial support of this work.

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The Crystal Structure of *m*-Tolidine

By F. Fowweather

Physics Department, College of Technology, Manchester 1, *England*

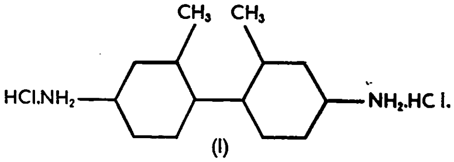
(*Received* 30 *May* 1951)

Standard single-crystal methods show that the unit cell of *m*-tolidine is orthorhombic, with $a = 7{\cdot}60$, $b = 14{\cdot}81$, $c = 21{\cdot}05$ Å; the cell contains eight molecules and has space group *Pcab*. The atomic co-ordinates are obtained by two-dimensional Fourier methods, together with the methods of steepest descents and error syntheses.

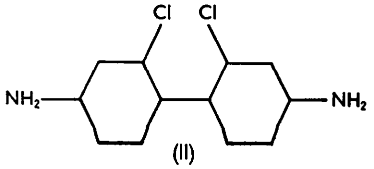
The two phenyl rings in each molecule are mutually inclined at an angle of 86°. The diphenyl link is 1·55 Å and the C–C bonds vary considerably with values between 1·31 and 1·41 Å. The structure is racemic with four right-handed and four left-handed molecules in the unit cell.

Introduction

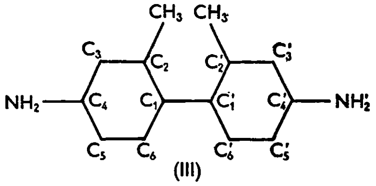
The work described is a contribution to a survey of a number of substituted diphenyls; a preliminary account of the survey has been given by Hargreaves & Taylor (1941). The structure of *m*-tolidine dihydrochloride (I) was determined by Hargreaves (1940) and refined by Fowweather & Hargreaves (1950). Smare (1948) determined the structure of 2-2'dichlorobenzidine (II).



(I)



(II)



(III)

Physical and X-ray data

m-Tolidine (III) is difficult to crystallize and forms soft, transparent rectangular plates, which cleave easily only parallel to the edge [010] of the plate face (001). The melting point is 89–90° C.

X-ray rotation, oscillation and Weissenberg photographs show that the crystals are orthorhombic with axial lengths

$$a = 7{\cdot}60 \pm 0{\cdot}03,\ b = 14{\cdot}81 \pm 0{\cdot}06 \text{ and } c = 21{\cdot}05 \pm 0{\cdot}1 \text{ Å}.$$

The density measured by flotation in a mixture of chloroform and alcohol is $1{\cdot}18 \pm 0{\cdot}01$ g.cm.$^{-3}$. There are eight molecules per unit-cell, giving a calculated density of 1·182 g.cm.$^{-3}$.

Absent spectra determine the space group to be $Pcab\text{–}D_{2h}^{15}$.

Zero-layer-line Weissenberg photographs were taken with Cu $K\alpha$ radiation, the crystal being rotated about the a and b axes. It was difficult to cut the soft crystals, and in addition the plates were thin, with a thickness