At high stearic acid concentrations this term is small, and within the limits of our experimental data sensibly constant for any particular value of Γ_2: however, at low concentrations it becomes quite appreciable as the plot of the values of Γ_1 against partial pressure of hexane shows (Fig. 3). The lower curve labeled $\Gamma_2 = 2G$ has been calculated according to Dean and Li[5] assuming the correction term to be negligible.

Figure 3 also includes the curve for $\Gamma_2 = 0$. Values for the adsorption of hexane on a clean water surface are higher than those reported by either Micheli or Cassell and Formstecher.[3,4] It is probable that the drop weight method used by these authors does not permit of sufficient time for the system to reach equilibrium. We find that at least 20 minutes are required to reach this equilibrium.

The maximum adsorption of hexane on a surface almost completely covered by stearic acid gives a limiting ratio of one molecule of hexane to one of stearic acid. It is interesting to note that the adsorption of hexane on stearic acid follows a type III isotherm at low acid concentrations going over to type V at high concentrations. Type V isotherms are usually explained on the basis of capillary condensation, an explanation that is hardly applicable in this case.

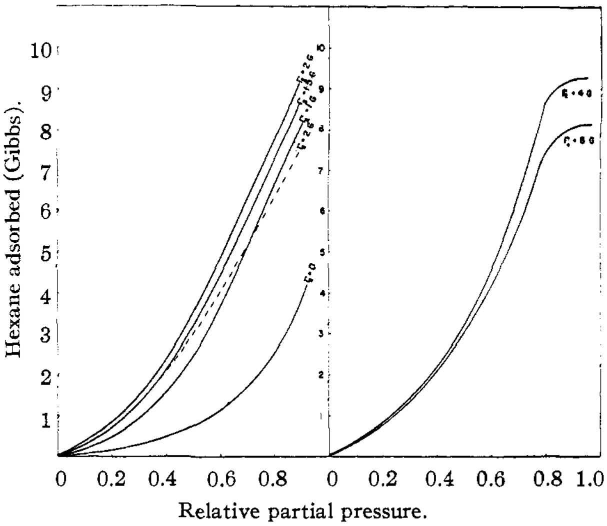

Fig. 3.—Adsorption isotherms for *n*-hexane on stearic acid monolayers at 30°.

EUGENE, OREGON RECEIVED APRIL 23, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Crystal Structure of Tetramethylpyrazine

BY DON T. CROMER,[1] AARON J. IHDE AND H. L. RITTER

Tetramethylpyrazine crystallizes from ether at room temperature in the orthorhombic class mmm, space group Pbca ($= D_{2h}^{15}$). Bounded Fourier projections of this crystalline species have been prepared from single-crystal X-ray diffraction data. The disposition of atoms within the unit cell has been determined and the several interatomic distances obtained. The molecule is planar, but the C–N bond length is apparently somewhat shorter than expected while the ring C–C bond appears to be longer.

As a contribution to the literature of crystal structures of simple heterocyclic compounds, we have made a complete structure determination of tetramethylpyrazine. The substance (m.p. 86°) was prepared according to the method of Kipping[2] and crystallized from anhydrous ether. The crystals usually grow in the tabular habit of truncated bipyramids, occasionally modified by a pair of prism faces. The regular octahedra mentioned by Brandes and Stöhr[3] for tetramethylpyrazine were never found in this Laboratory, and may be a polymorphic form. The morphology of our crystals indicates an orthorhombic class, mmm. If the pinacoid bevelments are assigned the form {111}, the axial ratios as determined by single-circle goniometer measurements are 0.902:1:1.104.

Single crystal rotation photographs around the three axes were prepared and the unit translations computed from layer line spacings. The approximate values so obtained were $a_0 = 8.45$, $b_0 = 9.38$, $c_0 = 10.30$ Å. The corresponding axial ratios agree sufficiently well with the goniometric data and these approximate lattice parameters served for the construction of reciprocal lattice nets and the indexing of X-ray reflections. The approximate density of the crystals was determined by displacement in a saturated solution of tetramethylpyrazine in isoamyl ether, as 1.08 g./cc. This gives 3.8 or 4 molecules per unit cell. Oscillation photographs over 10° ranges were taken using the multiple film technique of Robertson.[4] Crystals of 0.4 mm. maximum dimension were used. The very high vapor pressure of tetramethylpyrazine made it necessary to protect the crystals by a thin coat of varnish during exposure. Cu–K_α radiation was used with a Ni filter. All reflections were indexed, and the intensities estimated visually on an arbitrary scale and corrected in the usual way. No correction was made for absorption in the crystal.

More accurate values for the lattice parameters were obtained from selected oscillation photographs. Three of these photographs were found which carried symmetrically placed spots on the zero layer line. The centers of these films could thus be accurately fixed and the positions of the spots accurately measured. For rotation about the *a* axis and on the zero layer line

$$(k/b)^2 + (l/c)^2 = 2(1 - \cos x/2\pi r)/\lambda^2$$

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[1] National Lead Company, Titanium Division, South Amboy, N. J.

[2] F. B. Kipping, *J. Chem. Soc.*, 2889 (1929).

[3] P. Brandes and C. Stöhr, *J. prakt. Chem.*, **53**, 510 (1896).

[4] J. M. Robertson, *J. Sci. Instruments*, **20**, 175 (1943).

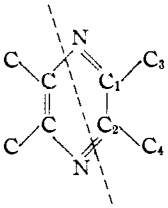
where x is the center-to-spot distance and r is the camera radius. A number of spots on the zero layer line were selected and b and c determined by least-squares. From the other films, a and b on the one film and a and c on the other were determined. The averaged results gave: $a = 8.35$, $b = 9.27$, $c = 10.62$ Å. with an average deviation of less than 0.01 Å. The corresponding axial ratios are 0.901:1:1.107.

There were 506 reflections observed and indexed out of a total of about 800 symmetrically distinct reflections possible. Of these, 319 were observed independently on oscillations about at least two different axes—81 about all three axes. If $F_i (i = a, b, c)$ represents the independently observed structure factors on a, b, c, oscillations, and F_u represents the average value actually used, an estimate of the agreement among duplicated observations may be obtained from

$$A = \frac{\Sigma|F_u - F_i|}{\Sigma F_u}$$

The summations are carried over every F that is observed more than once, as many times as observed. In this investigation, $A = 0.050$. The intensities observed covered the range from 1 to about 2500. Reflections were observed for $l \leqslant 13$, $h, k \leqslant 11$.

Examination of the observed reflections showed these systematic absences: $0kl$ when k is odd, $h0l$ when l is odd, and $hk0$ when h is odd. The space group is thereby unambiguously fixed as Pbca ($= D^{15}_{2h}$). Pbca has eight equivalent positions in the unit cell. With only four molecules in the cell, the repeating unit must be half of the centrosymmetrical molecule. Thus out of the 40 atoms (neglecting hydrogen) in the unit cell, only five atomic positions need be assigned. The choice of these five atoms and the labeling used here is shown in the diagram.



Assuming the molecule to be planar and the various bond lengths to have about the same values they have in similar compounds of known structure, and placing one molecule at each of the four symmetry centers of the Pbca cell, a trial structure was obtained essentially by the method of Pickett.[5] Structure factors calculated from this trial structure agreed sufficiently well with the observed intensities to permit assigning signs to 28 of the 43 observed F_{0kl}'s. In these early calculations of the structure factors, Robertson's[6] values for the atomic f's were used, giving C and N the same f.

A Fourier synthesis was made of the electron density of the unit cell projected on the yz plane, using these 28 F's. The resulting contour map showed that the trial structure was essentially correct. Following the usual procedure of refinement, successive syntheses eventually made it possible to assign signs to all the observed F_{0kl}'s. In all cases, peaks of electron density were located by the method of Booth.[7] The syntheses were carried out on the International Business Machines' 602-A computer and were evaluated at every sixtieth of the unit cell edge. A contour map of this projection is shown in Fig. 1. It will be seen from this projection that the y and z coördinates of all the atoms except one methyl carbon (C_4) may be determined. The C_4 methyl group lies almost directly above a methyl group from the molecule below and is not resolved.

Estimating the y and z coördinates of C_4 made it possible to carry out Bragg projections of the unit cell electron density on the xy and xz planes. In the final syntheses, it was possible to assign signs to all the observed F_{hk0}'s and F_{h0l}'s. The xy projection is shown in Fig. 2. All the x and y coördinates are determinable except those of C_1 and C_3. In the xz projection, the resolution is everywhere poor except for C_4. The z coördinate of C_4 was obtainable, however, and from the three projections fairly good values for all coördinates except x_{C_1} and x_{C_3} were obtained. These latter coördinates were fixed by line syntheses along the x axis through the (y,z) coördinates of C_1 and C_3.

Agreement among the same coördinates according to different projections was at this point not entirely satisfactory. Imperfect resolution and the small number of terms included in Bragg projections combine to make these projections less reliable than the more extensive bounded projections. Accordingly, bounded projections along the x and z directions were synthesized. Four projections of the contents of half the unit cell were made, two each of the yz and xy planes, using $-{}^1/_4 \leqslant x,z \leqslant +{}^1/_4$ and $0 \leqslant x,z \leqslant +{}^1/_2$ as the bounded ranges. Formulas for the bounded projected electron density were obtained by integration of the unbounded expressions given by Lonsdale.[8] The boundaries chosen both make the resulting expressions for the electron density particularly simple and ensure isolation of individual molecules. In calculating the F_{hkl}'s in connection with these syntheses, the approximate f's of Robertson were discarded and the atomic structure factors given in the International Tables[9] were used. A temperature factor was also introduced according to the method of Wilson.[10] Each F was multiplied by $\exp(-B \sin^2\theta/\lambda^2)$, where $B/\lambda^2 = 2.25$.

The bounded projection giving the best view of isolated molecules is that on the yz face where $-{}^1/_4 \leqslant x \leqslant {}^1/_4$. A contour map of this projection is given in Fig. 3. The coördinates obtained from the four projections are given in Table I. Disagreement among values given here can largely be assigned to the passage in some cases of a bound-

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(5) L. W. Pickett, *Proc. Roy. Soc.* (*London*), **142**, 659 (1933).

(6) J. M. Robertson, *ibid.*, **150**, 106 (1935).

(7) A. D. Booth, "Fourier Technique in X-ray Organic Structure Analysis," Cambridge, 1948.

(8) K. Lonsdale, "Simplified Structure Factor and Electron Density Formulae for the 230 Space Groups of Mathematical Crystallography," London, 1936.

(9) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Berlin, 1935.

(10) A. J. C. Wilson, *Nature*, **150**, 151 (1942).

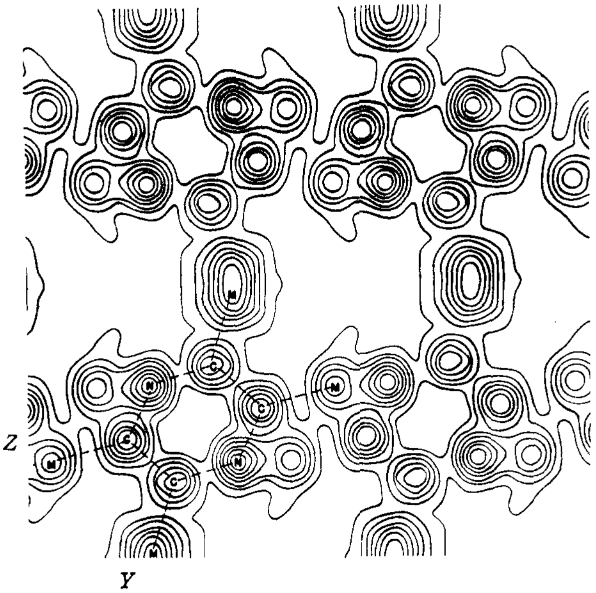

Fig. 1.—Unit cell contents projected on the yz plane. The contour intervals are equal but arbitrary.

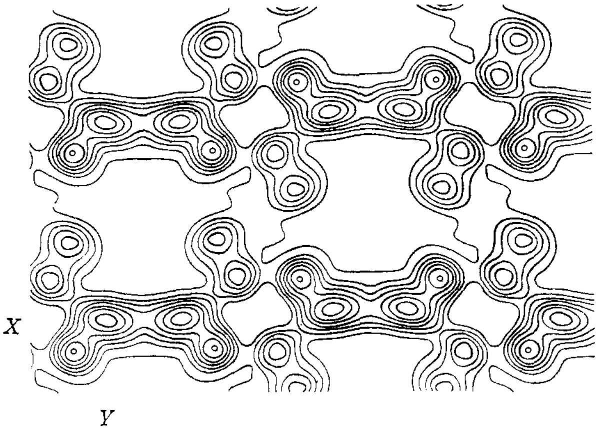

Fig. 2.—Unit cell contents projected on the xy plane. The contour intervals are equal but arbitrary.

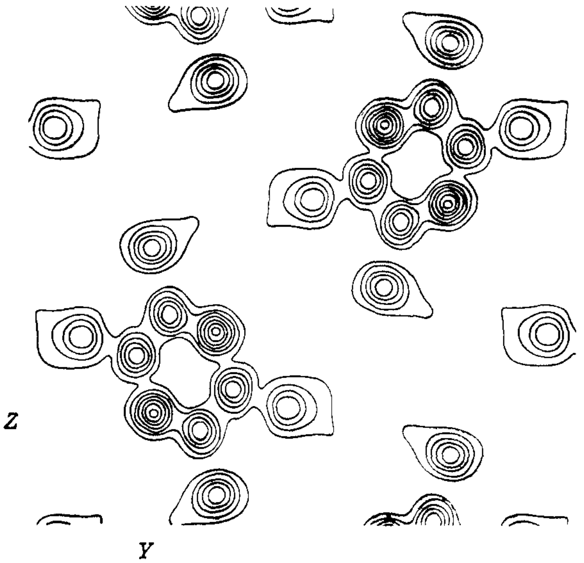

Fig. 3.—Bounded projection on the yz face for $-1/4 \leqslant x \leqslant +1/4$. Arbitrary but equal contour intervals.

ing plane too close to the atoms involved. This is a recognized source of distortion. Final coördinates for each atom were chosen from the projection(s) in which the bounding planes passed farthest from the atom. These values are given in Table II. In the single case of x_1, however, there appears to be no satisfactory choice. In one projection there is distortion from the bounding plane and in the other partial interference from a neighboring peak. For this single coördinate a line synthesis was made along x through y_1z_1 given by the other projections. The x coördinate of the peak obtained is included in Table II.

TABLE I

ATOMIC COÖRDINATES FROM THE FOUR BOUNDED PROJECTIONS, IN THOUSANDTHS OF THE UNIT CELL EDGE

	$-1/4 \leqslant x \leqslant +1/4$		$-1/4 \leqslant z \leqslant +1/4$		$0 \leqslant x \leqslant 1/2$		$0 \leqslant z \leqslant 1/2$	
Atom	y	z	x	y	y	z	x	y
C_1	139	032	014	138	139	034	004	143
C_2	041	104	−090	043	040	106	−088	044
C_3	297	067	020	299	296	071	019	300
C_4	086	222	−188	087	088	220	−181	089
N	095	−069	091	096	095	−067	090	096

TABLE II

FINAL VALUES OF THE ATOMIC COÖRDINATES

	In thousandths of unit cell edge			In ångström units		
Atom	x	y	z	x	y	z
C_1	010	139	032	0.083	1.288	0.328
C_2	−090	041	104	−0.752	0.380	1.067
C_3	020	297	067	0.167	2.753	0.687
C_4	−181	088	220	−1.511	0.816	2.257
N	092	096	−069	0.768	0.890	−0.708

From this set of atomic positions, all F_{hkl}'s, observed and unobserved, were calculated throughout the observable range. In order to compare the calculated F's with those observed, the latter were multiplied by a constant scale factor to convert them to an absolute scale. The method of Wilson[10] was found unreliable for this purpose, offering no definite choice within a rather wide range of values for the scale factor. The final scale factor was chosen by minimizing

$$R = \frac{\Sigma \| F_{\text{calcd}} | - sF_{\text{obsd}} |}{\Sigma sF_{\text{obsd}}}$$

with respect to s, the scale factor. The complete table of observed and calculated F's is available.[11] The corresponding value of the reliability criterion, R, is 0.23, within the range of acceptable agreement. It is interesting to note that a disproportionately large share of this discrepancy among the 506 observed reflections is due to the five strongest ones. If these five reflections—002, 102, 111, 200, 202—are omitted from R, its value is reduced to 0.19. Both the uncertain scale factor and evidence of secondary extinction probably justify this omission. It is worth noting further that omission of these five reflections from the minimization of R to obtain the scale factor would produce a scale factor giving an even lower value to R. This latter calculation was not carried out.

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(11) Order Document 3338 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

Geometry of the Molecule

From the coördinates in terms of fractions of the unit cell translations (Table II) and the best values of the unit cell translations themselves, the absolute coördinates of the atoms in Å. were computed. These values are also given in Table II. From them, the several interatomic distances may be computed.

The molecule appears to be planar. If the least-squares plane is passed through the origin and the five atoms whose coördinates are given in Table II, the mean distance of the atoms from the plane is only 0.009 Å. The bond angles are all 120° within ±2°. The several interatomic distances are $C_1C_2 = 1.44$; $C_1N = 1.30$; $C_2N = 1.32$; $C_1C_3 = 1.51$; and $C_2C_4 = 1.48$ Å. There is probably no significance to the difference between C_1C_3 and C_2C_4; and almost certainly no difference between C_1N and C_2N. Probable values for the several types of bond lengths in tetramethylpyrazine are selected as follows:

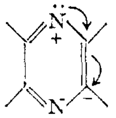
Ring carbon to ring carbon	1.44 Å.
Ring carbon to ring nitrogen	1.31 Å.
Ring carbon to methyl carbon	1.50 Å.

While it is difficult to assign probable errors to these values, the error analysis of Booth[7] is widely accepted. According to Booth, one may calculate the function

$${}_3R_2 = \frac{[\Sigma F_{\mathrm{obsd}} - |F_{\mathrm{calcd}}|]^2}{\Sigma F^2_{\mathrm{obsd}}}$$

carrying the summations over every observed F. The probable error, $\bar{\delta}$, in all of the coördinates is tabulated as a function of ${}_3R_2$ in reference 7. The value of ${}_3R_2$ in this work is 0.098, corresponding to a $\bar{\delta}$ of 0.060 Å. As Booth has pointed out, however, the contribution of very intense reflections to ${}_3R_2$ is disproportionately large; and when the large F's are unreliable, the resulting value of ${}_3R_2$ is unfairly high. Booth has suggested that these F's be weighted less heavily in computing ${}_3R_2$. If the five non-conforming reflections previously mentioned are omitted entirely from ${}_3R_2$, its value is reduced to 0.032. Perhaps a fair value of ${}_3R_2$ is about 0.07, giving a $\bar{\delta}$ of 0.025 Å. If the probable error in all atomic coördinates is $\bar{\delta}$, the propagated error in computed bond lengths is $\bar{\delta}\sqrt{2} = 0.035$ Å. The probable error we assign to the bond lengths deduced above is about 0.03 Å.

The ring carbon–carbon bond in tetramethylpyrazine seems therefore to be somewhat longer than the usual aromatic carbon–carbon distance (about 1.39 to 1.40 Å.). The aromatic carbon–nitrogen distance seems to be shorter than the usual value (about 1.35 to 1.36 Å.). The methyl-group-to-ring bond length is within the range of reported values (1.48 to 1.54 Å.). The difference appears to be real and may perhaps be due to resonance contributions from structures like



This electron shift would give more double bond character to the CN, and less double bond character to the CC, bonds in the ring. While this postulate is consistent with the apparent changes in bond length, it would seem that so much double bond character in both bonds of the C–N–C member would open the bond angle to considerably more than 120°. This bond straightening is not observed.

It is interesting to note that the closest approach of molecules in crystalline tetramethylpyrazine is nearly the same as in its benzene analog, durene. The smallest methyl-to-methyl (adjacent molecules) distances in durene are 3.87 and 3.93 Å. while in tetramethylpyrazine the corresponding distances are 3.84 and 3.72 Å.

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MADISON 6, WISCONSIN RECEIVED FEBRUARY 19, 1951