The C–H Distance in the Crystal Structure of Paraffins

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Abstract

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The C—H Distance in the Crystal Structure of Paraffins

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The electron-diffraction method for analyzing the atomic structure of crystals (as well as the neutron-diffraction method) now makes it possible to fix the positions of hydrogen atoms in crystals of organic compounds with an accuracy of about 0.02-0.03 Å (ˆ1). The classical method of structural analysis—X-ray diffraction—in the determination of hydrogen atoms gives a lower accuracy, about 0.10 Å. The application of electron diffraction and neutron diffraction makes it possible to find, as will be shown below, that the standard value of 1.08-1.09 Å usually adopted for the C—H distance undergoes systematic deviations in various compounds.

Paraffins $C_{nH_{2n+2}}$ are a convenient object for electron-diffraction analysis. As early as 1936 (ˆ2), an approximate estimate of the C—H distance was made by the trial-and-error method from data on the intensities of electron scattering; it led to the conclusion that this distance lies within the range 1.1-1.4 Å. In 1950 (ˆ3), application of Fourier synthesis of the potential gave a value of 1.17 Å for the C—H bond length; the accuracy of this investigation, in which a visual estimate of intensities and the multiple-exposure method were used, can now be estimated at approximately ±0.07 Å.

In the present work the paraffins $C_{18}H_{38}$ (I), $C_{30}H_{62}$ (II), and also a paraffin with m.p. 53.5° (III)—the same one that was studied earlier (ˆ3)—were investigated. The unit cells of all these paraffins in thin layers are, within the limits of error, practically identical; their periods a and b lie within the limits: a = 7.43-7.46 Å, b = 4.97-4.98 Å (ˆ4), and the projection of the pseudocell, which contains one zigzag of the carbon chain with period $c' = 2.53 \pm 0.02$ Å, has the same form. We restricted ourselves to studying only projections (from $hk0$ reflections), since the C—H distance is revealed here in an undistorted form.

The procedure of the investigation was as follows.

1) Recording electron-diffraction patterns with multiple exposures in transmission in the EG electron-diffraction apparatus (specimen—photographic-plate distance 700 mm, accelerating voltage 60 kV).
2) Determination of the unit cells.

Figure 1

Figure 1: Figure 1

3) Microphotometry of the $hk0$ rings of electron-diffraction patterns recorded in a position perpendicular to the beam (MF-4 microphotometer). Electron-diffraction patterns of this type are reproduced in (^{1},3). For each of the specimens (I, II, III), 2-3 of the best photographs were microphotometered and the results averaged. Weak distant reflexes (beginning approximately with $\sin\vartheta/\lambda = 0.45 \cdot 10^8$) were estimated visually from photographs with multiple exposures; the intensities of nearer, weak rings determined microphotometrically served as the standard for comparison.

4) Conversion from intensities to amplitudes by the formula

$$|\Phi_{hk0}| = \sqrt{I_{hk0}/d^2_{hk0}\rho},$$

where p is the repetition factor. In individual cases where two reflections coincided in one ring, the intensity was divided in the ratio observed in the point electron-diffraction patterns obtained, where each reflection is represented independently. The average discrepancy of the experimentally obtained values Φ_{hk0} for all three paraffins (I, II, III) can be calculated from the formula

$$R_{\text{exp}} = \sum_{hk} \left(\Phi^{\text{I}}_{hk0} - \Phi^{\text{II}}_{hk0}\right) \Big/ \sum_{hk} \Phi_{hk0}$$

(and analogously for II and III, I and III).

The sum in the denominator is normalized and is the same in all cases. The quantities R_{exp} have values of 8-12%, which may be regarded as an experimental estimate of the average accuracy of determining Φ_{hk0}.

5) Construction of Fourier syntheses of the projection of the potential $\varphi'(xy)$ onto the ab plane from Φ_{exp} with the calculated sign.

Fig. 1. **A**–Fourier projection of the potential of the paraffin pseudo-cell $C_{30}H_{62}$. Solid contour lines are drawn at intervals of 20 V · Å; the values at the dashed contour lines are indicated in V · Å. **B**–the corresponding difference projection, from which the C atoms have been removed and the remaining peaks represent H atoms. Contour lines are drawn at intervals of 5 V · Å.

6) Determination of the experimental atomic scattering curve of carbon, $f_{C\,\text{exp}}$, from the set of Φ_{exp}.

7) Calculation of the difference amplitudes $\Phi_{\mathrm{H}} = \Phi_{\mathrm{exp}} - \Phi_{\mathrm{C}}$, where Φ_{C} is the structural amplitude of carbon for the projection of the pseudo-cell with space group D_{2h}^{16}, equal to

$$\Phi_{\mathrm{C}} = 4 f_{C\,\mathrm{exp}} \cos 2\pi hx \cos 2\pi ky$$

for $h + k = 2n$, and equal to the same expression with sines for $h + k \neq 2n$.

8) Construction of difference syntheses

$$\varphi'_{\mathrm{H}}(xy) = \sum_{hk} \Phi_{\mathrm{H}} \exp[2\pi i(hx + ky)],$$

revealing only the H atoms, in order to exclude the influence of the C atoms on their position in the projection.

9) Determination of the positions of the C, H_1, and H_2 atoms by interpolation from the values obtained at the points of the synthesis (cell subdivision interval 1/60). In determining the position of the C atoms from the projection $\varphi'(xy)$, their mutual influence was taken into account.

10) Estimate of accuracy. The reliability factor for paraffin $C_{30}H_{62}$ was $R_1 =$ 11.5%, and the factors for the two other specimens were of the same order of magnitude. This quantity is close to $R_{\mathrm{exp}} =$ 8-12%; therefore it may be accepted that the accuracy of determining the amplitudes is not worse than 12%.

In Fig. 1 **A** and **B**, the complete and difference syntheses for $C_{30}H_{62}$ are given as examples.

The values obtained for the C–H distances are given in Table 1 (in Å). There is no reason to assume any real difference between

by the distances C–H_1 and C–H_2, and also by their difference in the paraffins studied. On average, the C–H distance proves to be equal to 1.12_3 Å. The maximum deviation of the observed values from the mean is 0.022 Å, the root-mean-square deviation 0.014 Å. On the other hand, one may estimate the accuracy of determination of the atomic coordinates from the accuracy of determining the amplitudes $b = 12\%$; then calculation of the mean square error of each separate measurement of the C–H distance by the formulas given in ([1,5]) gives 0.03 Å; for the totality of 6 such measurements,

$$\Delta r \simeq 0.03/\sqrt{6} = 0.012 \text{ Å}.$$

This value is close to the experimentally observed scatter, 0.014 Å. Summing all these data, one may accept that the root-mean-square error in the obtained distance 1.12_3 Å does not exceed 0.015 Å. In hexamethylenetetramine, for the

C—H distances of a tetrahedral carbon atom, electronographically 1.14 ± 0.10 Å (6) was found, by X-ray analysis 1.17 ± 0.1 (7) (an approximate estimate of the accuracy was made by us), and most accurately, by neutron diffraction (8), 1.13 ± 0.02 Å; in diketopiperazine, electronographically 1.10 ± 0.03 Å (1) was found. Although it would be desirable to have a higher accuracy of the individual determinations, nevertheless there is a definite tendency toward an increase of the usually accepted value 1.08—1.09 by approximately 0.04 Å. The data of the present investigation, as well as the work (8), confirm this most accurately.

Table 1

	Paraffin	Paraffin	Paraffin
	$C_{30}H_{62}$	$C_{18}H_{38}$	with m.p. 53.5°
$C—H_1$	1.12_1	1.14_0	1.10_2
$C—H_2$	1.14_0	1.12_7	1.11_2

At the same time, structural data for the C—H distance of carbon in an aromatic ring (see, for example, (9)) show that the observed distances are close to the standard value 1.08 Å. Consequently, there exists an influence of other bonds on the C—H distance. This influence is such that the presence of a smaller number, but stronger bonds of the C atom causes a shortening of the single C—H bond, i.e., evidently, some strengthening of it.

A full account of the present work, in the execution of which M. M. Stasova rendered great assistance to the authors, will be given elsewhere.

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