Reports of the Academy of Sciences of the USSR

A. I. KITAYGORODSKY and Yu. V. MNYUKH

1958

SovietRxiv

Fig. 1. R-subcell of a normal paraffin

Figure 1: Fig. 1. R-subcell of a normal paraffin

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1958. Vol. 121, No. 2

CRYSTALLOGRAPHY

A. I. KITAYGORODSKY and Yu. V. MNYUKH

TEMPERATURE CHANGES OF INTERMOLECULAR DISTANCES IN THE PARAFFIN n-$C_{30}H_{62}$. REFINEMENT OF THE SHAPE OF THE PARAFFIN MOLECULE

(Presented by Academician N. V. Belov, 13 III 1958)

1. For normal paraffins, two types of subcell* have been found experimentally –the rhombic (R) and the triclinic (T) ([1,2]). It is of interest to analyze carefully the packing of the molecules in both cases. The packing in the R-subcell, which is often encountered in structures formed by long-chain molecules (polyethylene, polyesters, paraffins, fatty acids, etc.), has features that until now have not been understood.

Figure 1 shows the plane xy of the paraffin subcell that is of interest to us, perpendicular to the axes of the molecular chains, and indicates the four shortest intermolecular H–H distances. Two of them ($H_1 - - - H_3$ and $H_2 - - - H_5$) lead, in the case of the paraffin n-C_{30}, to values of the intermolecular radius of the hydrogen atom $R_H = 1.21$ and 1.24 Å**, and these are larger than $R_H = 1.17$ Å, which is usually found in other molecular structures. The other two H–H distances are increased by 0.42 Å in comparison with $2R_H = 2.48$ Å. Meanwhile, the entire experience of organic crystal chemistry indicates the tendency of molecules to occupy a position corresponding to the maximum number of contacts between them (with intermolecular radii varying little from structure to structure) and to the absence of any significant "voids."

Fig. 1. R-subcell of a normal paraffin

2. Let us note that usually, in the absence of better data, one has to compare intermolecular distances in different

* The subcell is constructed on the repeat vectors of the methylene groups. For details see ([3]).
** At room temperature.

structures investigated at room temperature. However, thermal vibrations inevitably introduce some scatter into their values. A strict approach requires, when comparing, identical conditions, i.e., it requires the corresponding low-temperature data. In this connection, a study was undertaken of the temperature changes in intermolecular distances in the structure with an R-subcell, using paraffin n-C_{30} as an example. It was shown that: a) the parameters a_0 and b_0 of the subcell change anisotropically; b) as the temperature is lowered, the values of a_0 and b_0 tend toward limiting values of 7.20±0.02 Å and 4.86±0.02 Å, respectively; c) when the temperature is changed by more than 170°, no appreciable change occurs in the inclination of the plane of the molecular zigzag to the axes a_0 and b_0.

Table 1

Intermolecular distances in paraffin H-C_{30} at different temperatures (Å)

Intermolecular distance	+52°	+20°	−273° (extrapolation)
H_1—H_3	2.53	2.48	2.34
H_1—H_4	2.95	2.92	2.86
H_2—H_4	2.92	2.86	2.74
H_2—H_5	2.43	2.42	2.36

In Table 1 the intermolecular distances, measured at +52° and +20°, are compared with the corresponding distances obtained as a result of extrapolating the subcell parameters to limiting low temperatures. The table was compiled on the basis of a geometrical analysis carried out by graphical construction using the following parameters: interatomic distances C—H = 1.13 Å* and C—C = 1.53 Å, the distance between two neighboring valence-unbonded carbon atoms in the chain 2.54 Å, $\varphi_b = 41.2°$ and $\varepsilon = 109°30'$.

As is seen from the data presented, at low temperature the distances $H_1 - - - H_3$ and $H_2 - - - H_5$ lead to R_H = 1.17—1.18 Å, but the distances $H_1 - - - H_4$ and $H_2 - - - H_4$ remain greatly increased. In the literature we find extremely little information on the values of R_H at low temperature. It seems probable that the equilibrium distance of two valence-unbonded hydrogen atoms tends toward one and the same limit as the temperature is lowered. This limit of 2.35 Å apparently does not depend on the chemical nature of the carbon atom to which the hydrogen atom is attached, since the same limiting figure was also observed for naphthalene ([5]).

Fig. 3

Figure 2: Fig. 3

Fig. 2. Refinement of the shape of the paraffin molecule. Correction is shown in the shaded region. The intermolecular spheres of two neighboring valence-unbonded atoms overlap by more than 1 Å.

It remains to clarify the reason for the anomalous increase in the intermolecular distances $H_1 - - - H_4$ and $H_2 - - - H_4$. As is known ([4]), the theory of close packing at present is a first-approximation theory, according to which the shape of molecules is modeled by means of intermolecular radii, which are constants of the atoms. In constructing such models, the intermolecular spheres of neighboring valence-unbonded atoms sometimes overlap, as occurs in the case of the paraffin molecule

* According to recent electron-diffraction data of B. K. Vainshtein (personal communication).

(Fig. 2). The intermolecular distances H_1–H_4 and H_2–H_4 substantially exceed $2R_H$. Of course, there is nothing unusual in this; but is this scatter of distances accidental, i.e., specific to each crystalline structure, or is it a consequence of a difference between the shape of the molecule and the first-approximation shape that is obtained when universal average intermolecular radii are used? The search for the corresponding regularities is fully justified if one assumes that the refined shape of the molecule—and, moreover, the shape of the individual atomic groups—is a property of the molecule and not of the given crystalline structure.

Adhering to this point of view, we attempt to explain the increased values of the intermolecular distances discussed above by the specific shape of the carbon atoms of the methylene groups of paraffin. If it is assumed that, at the "junction" of two valence-unbound carbon atoms, the potential well is to a considerable extent "smoothed out" (Fig. 2), then this explains well the increase in the distances H_1–H_4 and H_2–H_4. There are no contacts between these atoms, but instead another contact is realized, as shown in the figure. It may be thought that such smoothing is associated with a redistribution of the electron density. The effect is as if the electron cloud were being "squeezed out" from the region of overlap.

Fig. 3. Comparison of the "ideal" and experimentally found T-subcell of paraffin. Subcell dimensions:
$b_{0\text{theor}} = b_{0\text{exp}} = 4.28$ Å ($b_{0\perp} = 4.08$ Å),
$a_{0\text{theor}} = 4.44$ Å, $a_{0\text{exp}} = 4.82$ Å,
$\gamma_{\text{theor}} = 102°$, $\gamma_{\text{exp}} = 107°$.
The reason for the discrepancy becomes obvious only after introducing a correction into the shape of the molecule.

3. Let us now analyze, from this same point of view, the triclinic subcell of

paraffin n-C_{18}. Fig. 3 gives a comparison of the "ideal" triclinic subcell, which was derived theoretically under the condition $R_H = 1.30$ Å and using the same parameters as in the case of the R-subcell, with the one found experimentally for paraffin n-C_{18} ([2]). Whereas the b_0 axes of the subcells practically coincide, the a_0 axis in paraffin C_{18} is larger by 0.38 Å. In addition, in the real cell the angle γ is larger by 5°. If we now make, regarding the shape of the molecule, the same assumption as in the case of the R-subcell, the reason for the discrepancy becomes clear. After refining the shape of the molecule it is found that steric hindrances (in the figure the overlapping regions are shaded) force the row of molecules I′, II′, ··· to move to a greater distance from the row I, II, ···, as a result of which the a_0 axis increases. At the same time the packing naturally tends to preserve the intermolecular H–H contact, marked in the figure by a heavy dot, and this leads to an increase in the angle γ. Thus, in order to avoid steric hindrances and preserve the mentioned H–H contact,

it is necessary to pass from the "ideal" lattice to the real one by "deforming" it along the arrow indicated in the figure. It is interesting to note that the distance H′–H″ for the real T subcell is increased, in comparison with $2R_H = 2.60$ Å, by 0.35 Å, a value close to that observed in the case of the R subcell.

4. Let us give examples that support the refinement of the molecular shape made above.

Fig. 4. *a*–Hypothetical structure of iodoform with non-close packing in the *ab* layer. *b*–Structure of iodoform in the *ab* layer. Contacts J–J: 1—1′ = 3.98 Å, 1—2′ = 4.34 Å. Introducing a correction into the molecular shape naturally explains the packing found experimentally.

A. Normal fatty acids. Fatty acids preserve the main features of the packing characteristic of paraffins. However, the formation of hydrogen bonds, as well as the steric difficulties introduced by the COOH group, lead to the packing of aliphatic chains often deviating from the "paraffin" one. This is expressed, in particular, in the fact that molecular displacements cease to be integral multiples of c_0. Analysis of the available data ([6]) on fatty acids shows that the mutual shift of molecules related by the translation b is in all cases an integer number of "stories" (1 "story" = c_0). At the same time, the shift of molecules related by the translation a, in most cases, is a fractional number of "stories." This means that in the second case the contact between molecules is less strong, since it is much more easily disrupted as soon as any steric difficulties arise for packing molecules in an R- or T-subcell of the paraffin type. This argues in favor of the absence of deep "depressions" in that section of the molecule which coincides with the plane of the aliphatic zigzag, confirming the assumption made above that refines its shape.

B. Pentadecanoic acid CH_3—$(CH_2)_{13}$—COOH. One of the modifications of pentadecanoic acid has a T subcell with parameters $a = 5.01$ Å and $b = 4.25$ Å ([6]). In this case as well, the parameter a is anomalously increased for the reason

discussed in detail for the paraffin n-C_{18}.

C. Iodoform CHJ_3. It may be thought that corrections to the molecular shape analogous to that which was made for the aliphatic zigzag of carbon atoms can also be made in all other cases where, in the molecule, neighboring atoms not bonded by valence approach one another to a distance considerably smaller than the sum of the intermolecular radii. In iodoform, the shortening of the J—J distance within the molecule is 0.44 Å. Fig. 4 shows a hypothetical packing of molecules in a layer (A) and that found experimentally (B) ([7]). In the second case, the distance between atoms 1 and 2′ is increased in comparison with $2R_J$ = 4.0 Å by 0.34 Å. The difference is easily explained if an appropriate correction is introduced into the shape of the iodoform molecule (as conventionally shown in Fig. 4B) at the places where the atoms are compressed. In the same places where this compression is absent, the iodine atoms (1 and 1′) touch one another.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
7 III 1958

CITED LITERATURE

1. C. W. Bunn, Trans. Farad. Soc., **35**, 482 (1939).
2. A. Müller, K. Lonsdale, Acta Cryst., **1**, 129 (1948).
3. A. I. Kitaigorodskii, Kristallografiya, **2**, 646 (1957).
4. A. I. Kitaigorodskii, *Organic Crystal Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1955.
5. V. M. Kozhin, A. I. Kitaigorodskii, ZhFKh, **29**, 1897 (1955).
6. E. von Sydow, Ark. f. kemi, **9**, 231 (1956).
7. T. L. Khotsyanova, A. I. Kitaigorodskii, Yu. T. Struchkov, ZhFKh, **27**, 647 (1953).

Note: Figure translations are in progress. See original paper for figures.