568

Inclusion Compounds in Perhydrotriphenylene. Part II.[1] The Conformation of the Included Molecules

By G. Allegra, M. Farina, A. Colombo, G. Casagrande-Tettamanti, U. Rossi, and G. Natta, Istituto d Chimica Industriale del Politecnico di Milano, and Centro Nazionale di Chimica delle Macromolecole del C.N.R. Sezione I, Milano, Italy

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION B
Physical Organic Chemistry

1967

Inclusion Compounds in Perhydrotriphenylene. Part II.[1] The Conformation of the Included Molecules

By G. Allegra, M. Farina, A. Colombo, G. Casagrande-Tettamanti, U. Rossi, and G. Natta, Istituto d Chimica Industriale del Politecnico di Milano, and Centro Nazionale di Chimica delle Macromolecole del C.N.R. Sezione I, Milano, Italy

X-Ray rotating-crystal photographs of perhydrotriphenylene (PHTP) inclusion compounds show the presence of continuous streaks due to interference from the included molecules; from their spacings the molecular repeat distance can be measured. The chain conformation of n-hydrocarbons is not completely *trans*-planar, although it tends to planarity with increasing molecular weight. This phenomenon has been interpreted quantitatively by assuming a statistical distribution of the molecules between the *trans*-planar model and a twisted conformation represented by the ...TGTG'TGTG'... sequence of internal rotation angles (T = *trans*, G = *gauche* +, G' = *gauche* −). An analogous investigation has shown that included monocarboxylic acids are dimeric, and that in dialkyl ether molecules the C–O–C groups enter largely into the molecular twisting. In both cases, the alkyl groups have conformations similar to those in the pure hydrocarbons. An eclipsed conformation is suggested for included 2,2,4-trimethylpentane.

We here describe a detailed study of the conformation of linear saturated hydrocarbon molecules included in *trans,anti,trans,anti,trans*-perhydrotriphenylene (PHTP). We discuss some qualitative conclusions about included linear ethers and monocarboxylic acids, and of a non-linear hydrocarbon (2,2,4-trimethylpentane) The experimental data are derived from the *X*-ray diffraction effects due to the rows of molecules included

---

[1] Part I, G. Allegra, M. Farina, A. Immirzi, A. Colombo, U. Rossi, R. Broggi, and G. Natta, preceding Paper.

in the channels; in this respect our study is analogous to those of other workers [2-4] on urea and thiourea inclusion compounds. However, *X*-ray spectra of the adducts has led to our more detailed conclusions about the molecular conformations of the guest compounds.

Linear Hydrocarbons Included in Perhydrotriphenylene.—(a) *Experimental data and general remarks.* On the *X*-ray rotating-crystal photographs, along the *c*-axis (parallel to the channels), continuous streaks [2-4] due to the infinite rows of hydrocarbon molecules were detectable in a limited range of values of the ζ reciprocal co-ordinate, extending approximately from 0 to 0·2 Å^{-1}. By repeated measurements on different specimens, the standard error in each case was reduced to *ca.* ± 1%. The repeat distances for hydrocarbons C_nH_{2n+2} (*n* 5—24) are in Table 1.

TABLE 1

Observed repeat distances along the channel axis of included n-hydrocarbons ($C_nH_{2\,n+2}$)

n	5	6	7	8	9	10	11
p_n (Å)	8·32	9·43	10·69	12·00	12·98	14·36	15·67
n	12	13	14	16	18	20	22
p_n (Å)	16·80	18·00	19·24	21·58	24·24	27·13	29·18
n	24						
p_n (Å)	31·98						

The absence of discrete spots on the diffraction streaks shows that there is no coherence between host and guest molecules (see Plate 1 in ref. 1). The smoothness of the plot of the repeat distances against *n* (the number of carbon atoms per hydrocarbon molecule) further proves the absence of any relevant effect induced by the crystalline environment upon the molecular conformation of particular hydrocarbon terms, such as could arise by rational numbers of included molecules per host molecule.[2,5]

(b) *Non-planar conformation of the included molecules.* Assuming a planar zig-zag conformation, normal values for bond lengths and angles (C-C = 1·54 Å, C-C-C = 112°), and that the molecular skeleton is parallel to the channel axis, the analytical relationship which links the repeat distance $p_n{}^\circ$ along the channel axis between neighbouring hydrocarbon molecules, with *n*, is (Figure 1):

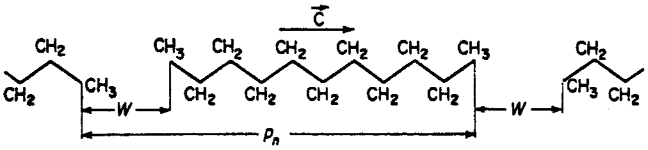

FIGURE 1 Scheme showing the meaning of p_n and W for a sequence of included C_nH_{2n+2} n-hydrocarbon molecules, in the *trans*-planar conformation

$$p_n{}^\circ(\text{Å}) = 1{\cdot}275(n-1) + W \qquad (1)$$

where *W* is the axial projection of the C · · · C distance between methyl groups at van der Waals contact.

In Figure 2 the shortening (Δp_n) of the observed repeat distances with respect to the values given by equation (1) is plotted against *n*. The value of *W* has been temporarily assumed 3·65 Å; we will further discuss this choice. In the range C_5—C_{16} the best straight line through the experimental p_n values has the equation:

$$p_n(\text{Å}) = 1{\cdot}215(n-1) + 3{\cdot}44 \qquad (2)$$

where the slope [the coefficient of $(n-1)$] has a standard error less than 0·01 Å. The experimental slope is therefore considerably less than that expected for the *trans*-planar conformation.

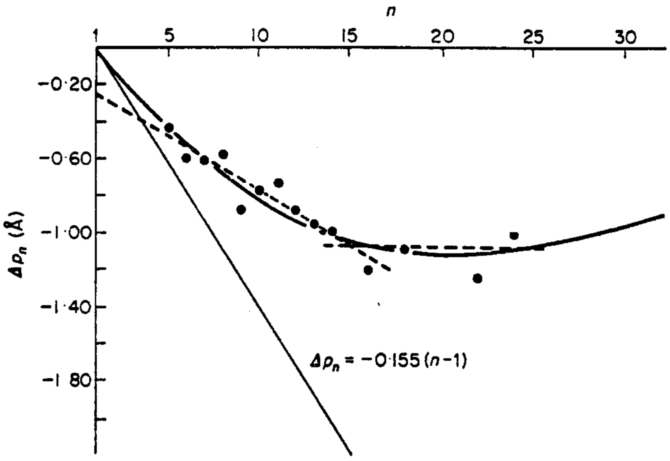

FIGURE 2 Plot showing the shortening of the repeat distances of normal hydrocarbons with respect to the calculated value for the zig-zag planar conformation [see equations (1) and (4), where W = 3·65 Å] against *n*, the number of chain carbon atoms.

The black spots correspond to the experimental values; the best fitting straight lines are broken; the continuous curve corresponds to equation (5). The lowest straight line, through the origin, refers to the completely twisted conformation ($f_n = 1$)

This effect cannot be attributed to a tilt of the molecular plane with respect to the channel axis; in fact, the angle of tilt should diminish with increasing *n*, thus causing an increase (and not a decrease) of the slope with respect to 1·275 Å. Careful examination of the fitting of rigid molecules in the full *trans* conformation inside the channels [see Figure 4(a)] shows that the maximum tilt should cause a shortening of ~0·10 Å for p_5, with rapidly decreasing values for higher hydrocarbon terms. Since this amount is comparable with the experimental errors involved, we neglect any consideration based on the molecular tilt in the following discussion.

We conclude, therefore, that a conformation less extended than the zig-zag planar one is to be attributed to the hydrocarbon chains. The same conclusion could be reached by considering the exceedingly low values of *W* obtained by fitting equation (1) to some experimental

---

[2] A. E. Smith, *Acta Cryst.*, 1952, **5**, 224.

[3] H. U. Lenné, *Acta Cryst.*, 1954, **7**, 1.

[4] N. Nicolaides and F. Laves, *J. Amer. Chem. Soc.*, 1958, **80**, 5752; F. Laves, N. Nicolaides, and K. C. Peng, *Z. Krist.*, 1965, **121**, 258.

[5] H. U. Lenné, *Z. Krist.*, 1961, **115**, 297.

values of p_n; as an example, $p_{16} = 21{\cdot}58$ Å, and the corresponding value of W is 2·46 Å, which is clearly too short to have acceptable $CH_3 \cdots CH_3$ distances.

For hydrocarbon terms C_nH_{2n+2} with $n > 16$, there is a marked increase in the slope (Figure 2), which seems to approach, within experimental errors, 1·275 Å, thus pointing at a progressive attainment of the planar conformation. This is further confirmed by the X-ray diagrams of the inclusion compounds with $n \geqslant 30$, where there is an addition broad streak, the more marked the greater n, at $\zeta = 1/(2{\cdot}55 \pm 0{\cdot}02)$ Å^{-1}, corresponding to the polyethylene repeat in the fully extended conformation. As additional arguments, the X-ray refinement on the ($hki0$) reflections of some PHTP–n-hydrocarbon adducts has revealed that the C atoms of the included molecules are disposed on the average on cylinders of different radii, regularly decreasing with increasing molecular length. As an example, the plot of the disagreement factor against the cylinder radius shows a fairly sharp minimum corresponding to $0{\cdot}65 \pm 0{\cdot}03$ and $0{\cdot}47 \pm 0{\cdot}03$ Å for n-heptane and n-C_{36}, respectively (compare with the theoretical value of 0·43 Å for the fully extended molecule). Moreover, the a unit cell shows a shortening of about 0·10 Å from n-heptane to n-C_{36}.

(c) *Possible conformational models of the included molecules. Partition between planar and twisted conformations.* We have tried to define a suitable conformational hypothesis in order to interpret the two fundamental conclusions derived from experiment: (i) the deviation of the included hydrocarbon molecules from the *trans*-planar conformation; (ii) the trend towards greater planarity with increasing chain length, which leads to complete planarity for large n.

One could first suppose that, because of the energy stabilisation due to the channels, the chain conformation is different from the *trans*-planar one, and identical for all the included molecules. However, it is very difficult on these grounds to understand why the conformation should vary with the chain length.

But even a linear succession of molecules assuming two or more different conformations may give rise to interference effects, provided that the spacings between neighbouring molecules are not very different; in such a case the diffraction streaks must show a tendency to vanish more rapidly than the diffraction spots with increasing ζ co-ordinate.* This is what is observed: in no case is any streak observable at $\zeta > 1/5{\cdot}0$ Å^{-1}, with the sole exception of the streak at $\zeta = 1/2{\cdot}55$ Å^{-1}, which is due to intramolecular effects, as shown before. The position of the diffuse streaks gives the average value of the molecular repeat distance.

We have supposed therefore that the included molecules assume different conformations, in a random sequence; their probability of occurrence should be governed both by the steric hindrance with the channel walls, and by the conformational energy. According to the latter factor, we first restricted our analysis to molecular models characterised by 'staggered' conformations (*trans* and *gauche*) of chain carbon atoms, and then checked their degree of fitting inside the channels. We will introduce in the following the notations T, G, and G′ for a *trans* ($\sigma = 180°$), a *gauche plus* ($\sigma = 60°$), and a *gauche minus* ($\sigma = 300°$) conformation, respectively.

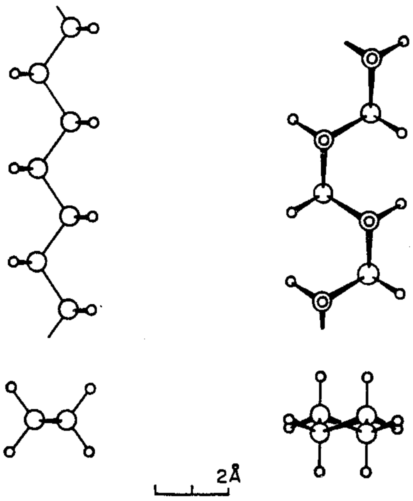

FIGURE 3 Side and end view of the (. . . TTTT . . .) (left) and of the (. . . TGTG′ . . .) (right) conformation of a n-hydrocarbon sequence

The most suitable molecular conformations may be described as:

Model A: . . . TTTTTTTTTT . . . (*trans*-planar conformation).

Model B: . . . TGTG′TGTG′ . . . (twisted conformation).

The molecular models are represented in Figure 3; the average chain repeats per methylene unit are 1·275 and 1·120 Å for A and B, respectively.

In Figure 4 (a) and (b) the fitting of the above models inside the channel is represented at three different channel levels, putting into effect the van der Waals shapes of the molecules; the hydrogen radius is 1·20 Å,[6] and in every crystal site the presence together of two enantiomorphous PHTP molecules has been considered, according to the $P6_3/m$ space group.[1] Both models may be fitted into the channel, at any level, with only slight compression of the van der Waals spheres.

Any other simple chain conformation has been discarded; for example, Figure 4(c) shows that the chain model corresponding to a . . . TGTG . . . or

---

* By considering the system under investigation as a one-dimensional array of molecules with different conformations in a random sequence, we may apply to the average X-ray scattered intensity the results already given for one-dimensionally disordered systems [see, *e.g.*, expression (28) in G. Allegra, *Acta Cryst.*, 1965, **17**, 579]. If two conformations in a 1 : 1 ratio are assumed with (approximately) the same scattering form factor, and a difference of 10% between their repeat distances, the calculations show that the first two streaks should be clearly detectable, while the next ones should rapidly broaden and vanish.

[6] L. Pauling, 'The Nature of the Chemical Bond,' Cornell Univ. Press, 3rd edn., 1960, p. 260.

. . . TG′TG′ . . . sequence (a threefold helix) is clearly unsuitable for the fitting into the channels, although its intramolecular energy is practically identical with that of model B. All other molecular models characterised by staggered conformations fulfil even less requirements.

From the above we concluded that the most likely picture of the phenomenon should be given by a Boltzmann distribution between the A and B molecular conformations. We then investigated our hypothesis quantitatively. Assuming the zero energy level to correspond to the *trans*-planar conformation, we expressed as ΔE the energy contribution due to every *gauche* conformation. Its value is not expected to be identical with the usual $CH_2 \cdots CH_2$ *gauche* interaction (0·5—0·8 kcal./mole);[7] it may be altered both by the effect of the van der Waals interactions with the channel walls and by the free-energy gain resulting from the more complete filling of the channels permitted by the twisted conformations. At least the latter effect should certainly reduce the above figure; ΔE is consequently to be regarded as a free-energy parameter. Although it could be slightly different for different hydrocarbon terms, its constancy has been assumed.

We attributed the same number of *gauche* bonds, *i.e.*, $(n - 3)/2$, to the twisted conformation of all hydrocarbon terms, regardless of whether n is even or odd; as we shall see, the resulting value of ΔE is sufficiently low to make the involved error negligible.

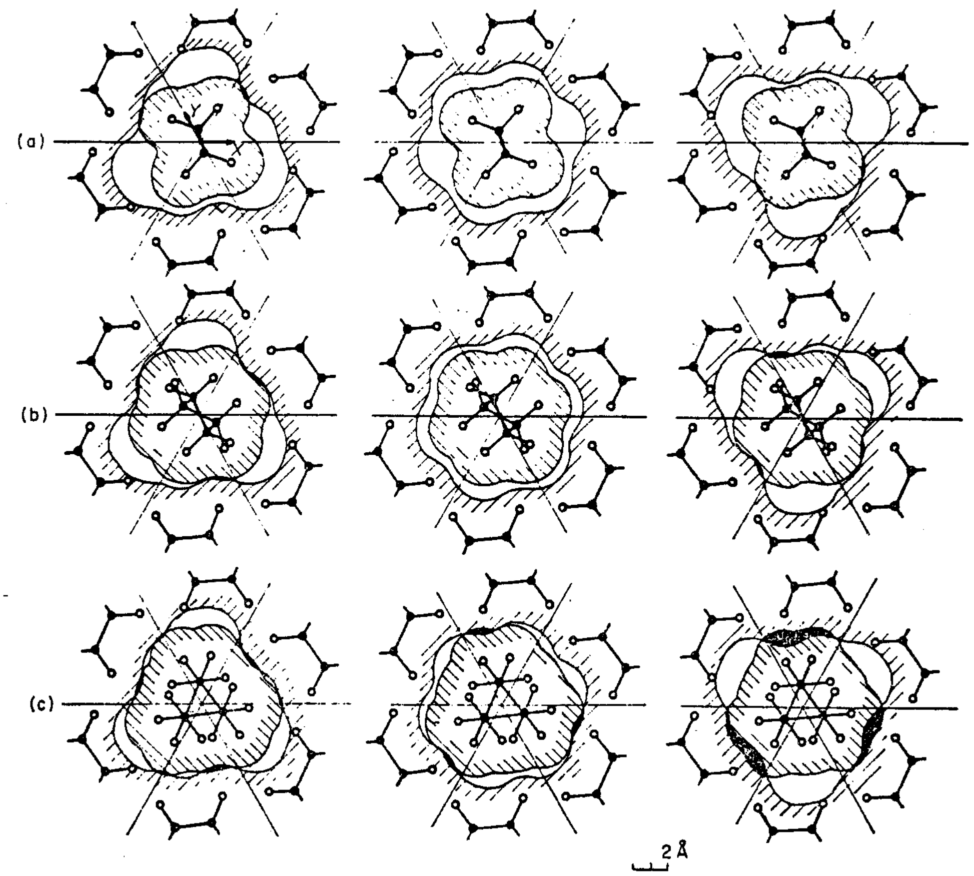

FIGURE 4 Fitting of the n-hydrocarbon molecules into the PHTP channels at levels $z = -\frac{1}{4}c$; $z = 0$; $z = +\frac{1}{4}c$ (from left to right), viewed along the channel. The channel contours correspond to the envelope of the van der Waals spheres of hypothetical hydrogen atoms contacting the host molecules.

In (a), (b), and (c) the (. . . TTTT . . .), (. . . TGTG′), and (. . . TGTG . . .) conformations, respectively, are shown together with their external van der Waals shapes. The molecular axis coincides with the channel axis; the orientation is the same at all the levels, and it has been so chosen as to give rise to the least host–guest interactions

The statistical weights of the planar and of the twisted molecular conformations are 1 (standard of reference) and $K \exp[-\Delta E(n - 3)/2\boldsymbol{R}T]$, respectively. K is a normalising factor which accounts both for the degeneracy of the twisted model, which may start from one end as TG . . ., or TG′ . . ., or GT . . ., or G′T . . ., and for its different freedom in rigid rotation inside the channels.

The fraction of twisted molecules (f_n), and the average repeat distance (the experimental value) are given by:

$$f_n = Ky^{n-3}/(1 + Ky^{n-3});\ y = \exp(-\Delta E/2\boldsymbol{R}T) \quad (3)$$

$$\begin{aligned} p_n &= [1{\cdot}120f_n + 1{\cdot}275(1 - f_n)](n - 1) + W \\ &= 1{\cdot}275(n - 1) - 0{\cdot}155f_n(n - 1) + W \quad (4) \end{aligned}$$

---

[7] G. J. Szaz, N. B. Sheppard, and D. H. Rank, *J. Chem. Phys.*, 1948, **16**, 704; L. S. Bartell and D. A. Kohl, *ibid.*, 1963, **39**, 3097.

We determined W by considering that, for steric reasons, the facing methyl groups of neighbouring molecules keep at opposite ends of the channel diameter; from its average value (~5·8 Å), and the van der Waals radius of the methyl groups (2·03 Å),[8] the resulting figure is $W = 3{\cdot}65$ Å. Figure 2 shows the best line corresponding to Δp_n [see (1) and (4)]:

$$\begin{aligned}\Delta p_n = p_n - p_n{}^{\circ} &= -0{\cdot}155 f_n(n-1) \\ &= -0{\cdot}155(n-1)[Ky^{n-3}/(1+Ky^{n-3})] \quad (5)\end{aligned}$$

where $K = 2{\cdot}5$ and $y = 0{\cdot}915$. The agreement with the observed data is satisfactory.

From the above value of y and expression (3), the resulting figure for ΔE (at room temperature) is 0·11 kcal./mole. Since this value is affected by our previous choice of W, we have also carried out best-fit calculations for $W = 3{\cdot}55$ and 3·75 Å, which correspond to a displacement of neighbouring CH_3 groups along the channel diameter of 1·97 and 1·56 Å, respectively; these figures should be considered as close to the limiting values. Correspondingly, ΔE is 0·16 and 0·08 kcal./m.u. in the two cases; as an overall result, $E = 0{\cdot}12 \pm 0{\cdot}05$ kcal./mole.

Molecular Conformations of Included Ethers and Monocarboxylic Acids.—We applied the previous results to a less sophisticated investigation of inclusion compounds of ethers and monocarboxylic acids, where the guest molecules still contain CH_2 sequences of varying length. Confining our analysis to molecules containing alkyl groups up to 11 carbon atoms, we obtained the repeat distances in Table 2. The data are consistent with the following best-fit linear relationships:

TABLE 2

Observed repeat distances along the channel axis of included n-ethers ($C_nH_{2n+1}OC_nH_{2n+1}$) and monocarboxylic acids ($C_nH_{2n+1}COOH$)

Ethers

n	3	4	5	6	8
p_e (Å)	9·72	12·11	14·80	17·18	22·43

Acids

n	4	5	7	11
p_a (Å)	16·60	19·26	23·93	33·60

$C_nH_{2n+1}OC_nH_{2n+1}$

$$p_e(\text{Å}) = 2{\cdot}43_4(n-1) + 5{\cdot}08 \quad (6)$$

$C_nH_{2n+1}COOH$

$$p_a(\text{Å}) = 2{\cdot}44_4(n-1) + 9{\cdot}48 \quad (7)$$

From expression (7) it is apparent that the included acid molecules are dimeric, as they are in other states of aggregation; the same conclusion is reached from analytical determinations of the carboxyl groups[1] which are in excellent agreement with the above equation. Moreover, the above expressions show that the same shortening of the chains with respect to the fully extended conformation still occurs in ethers and monocarboxylic acids.

From a comparison of the repeat distances of ethers and acids with those of the corresponding n-hydrocarbons, we derived the components along c of the distances between carbon atoms linked by oxygen bridges (in ethers) or belonging to hydrogen-bonded carboxyl groups (in acids). They are labelled l for ethers and l' for acids (Figure 5).

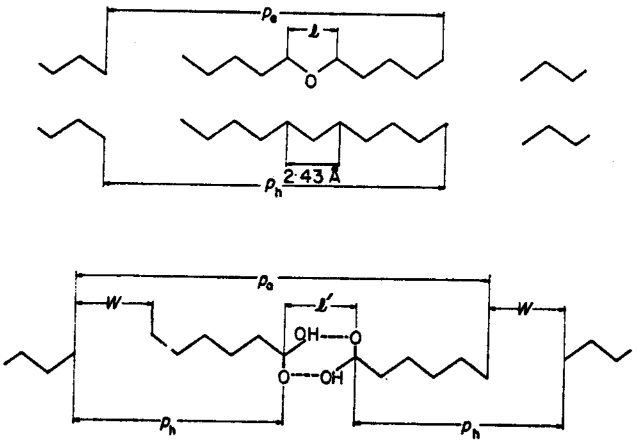

FIGURE 5 Schematic representation of the relationships between the repeats along the channel of the C_n–O–C_n ether molecules and of the C_{2n+1} hydrocarbons (upper part), and between the $(C_{n-1}COOH)_2$ acid dimers and the C_n hydrocarbons (lower part)

In the case of ethers we deduced the value of l by comparison between the repeat distances p_e and p_h of a given ether and the n-hydrocarbon with the same number $(2n + 1)$ of heavy skeleton atoms [see equation (2)]; from Figure 5 the following relationship results:

$$l = p_e - p_h + 2{\cdot}43; \text{ where } p_h = 2{\cdot}430(n-1) + 5{\cdot}87 \quad (8)$$

2·43 Å being the average projection value of the C · · · C distance between atoms separated by two bonds in the reference hydrocarbons.

In the case of acids, the comparison was between their repeat distances (p_a) and those (p_h) corresponding to the hydrocarbon terms with the same number (n) of carbon atoms per molecule. From Figure 5 the relationship which gives l' is:

$$l' = p_a - 2p_h + W \quad (9)$$

where W has been taken equal to 3·65 Å.

From (2), (6), (7), (8), and (9), we obtained 1·64 Å and 3·81 Å for l and l', respectively.

As for l, the resulting value is significantly less than that expected for the extended conformation of the (C–O–C) groups (2·34 Å; if C–O = 1·43 Å and C–C–C = 110°), suggesting that they are largely involved in the molecular twisting.

As for l', its value is not different, within the accuracy limits, from the distance between carbon atoms of dimeric carboxyl groups, as quoted from X-ray single-crystal studies (3·89 Å).[4] It is to be concluded that the large steric interaction between the carboxyl groups and the

---

[8] P. W. Teare, *Acta Cryst.*, 1959, **12**, 294.

walls of the channels binds the C · · · C vector at a small angle to the channel axis.

The Molecular Conformation of 2,2,4-*Trimethylpentane*.—We observed that some relatively bulky molecules, such as 2,2,4-trimethylpentane can be included in PHTP, although with a lower stability than linear hydrocarbons.

The value of the molecular repeat is 8·65 Å, *i.e.*, slightly higher than of n-pentane (8·32 Å). This may be explained by considering that twisting of the iso-octane molecules cannot lead to any considerable decrease in the molecular length, owing to the presence of bulky groups (a t-butyl and an isopropyl group) at the ends.

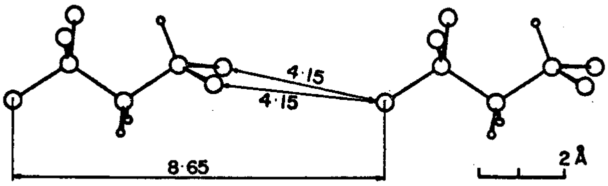

FIGURE 6 Molecular conformation and mutual disposition of neighbouring molecules of 2,2,4-trimethylpentane in the inclusion state. The larger spheres represent carbon atoms, and the smaller ones hydrogen atoms; primary hydrogen atoms have been omitted

The best fitting molecular conformation is represented in Figure 6; it seems also to satisfy at best the conformational energy requirements. In particular, the 'eclipsed' conformation around the CH_2–$CH(CH_3)_2$ bond avoids any *syn*-diaxial interaction of methyl groups.

Figure 6 also shows a possible mode of succession of the neighbouring molecules inside a channel; the observed repeat distance (8·65 Å) agrees well with the proposed model, since the resulting $CH_3 \cdots CH_3$ intermolecular distances (4·15 Å) are quite reasonable.

Conclusions.—The *X*-ray conformational analysis of PHTP-included n-hydrocarbon molecules leads to the following conclusions. (*a*) The short molecules are appreciably twisted; the degree of twisting tends continuously to zero for increasing molecular length. (*b*) The conformation of the twisted molecules should be closely represented by the (. . . TGTG′TG . . .) model (Figure 3). (*c*) Every molecule is either in the twisted or in the *trans*-planar conformational state. Intramolecular inversions should involve an appreciable energy (~2·5 kcal./mole from our calculations [9]); moreover they should cause an appreciable shortening of the long molecules, contrary to experiment. (*d*) The energy difference between *gauche* and *trans* conformations is certainly much lower than for the molecule in the free state.

The above conclusions could also be applicable to the ωω′-dicyclohexylalkanes included in thiourea, studied by Lenné.[3]

We think that similar methods of conformational analysis could help in many instances. Although the conformation in the inclusion state is generally different from that of the isolated molecule or from that which might occur in a chemically homogeneous crystal, analogous situations, such as the adaptation of the molecule to a template, represent widespread and important cases. Some aspects of the selectivity of the heterogeneous catalysis can be related to the mode of approach of the reagent to the active centre. Even with reactions that occur in the homogeneous phase and are promoted by rigid molecules, useful information could be obtained from the study of appropriate inclusion compounds. We refer to some types of biochemical reactions, in particular to enzymic reactions. The studies by Cramer [10] on the reactions promoted by cyclodextrins seem informative in this respect.

[6/1570 *Received, December* 12*th*, 1966]

---

[9] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, 1966, **44**, 3054.

[10] F. Cramer and W. Kampe, *J. Amer. Chem. Soc.*, 1965, **87**, 1115; N. Hennrich and F. Cramer, *ibid.*, p. 1121.