but no appreciable absorption above 2800 Å. Therefore the absorption observed in toluene is probably due to a complex between $SnCl_4$ and toluene and may be due to a charge transfer process of the type described by Mulliken.[22]

The Exchange of Tritium between TCl and Mesitylene.—Fifteen cells were filled with mesitylene and tritiated HCl. All the cells showed some decrease in the specific activity of the HCl even after the 10% correction for exchange with the walls at 140°. The rate of loss of the tritium was not reproducible. Values of k' ranged from 10^{-5} sec.$^{-1}$ to 3×10^{-4} sec.$^{-1}$ at 140°. The mesitylene exchange is apparently even more sensitive to traces of catalytic impurities than the toluene exchange.

Five of the cells, of which one was not heated above room temperature and four were heated at 140° for times up to 225 min., gave values of about 0.8 for S/S_0, and no higher values were obtained at 140°. This suggests that there is an impurity in the mesitylene which undergoes rapid exchange with TCl, while the mesitylene itself exchanges very slowly if at all in the absence of other impurities. One mole of an impurity with one exchangeable hydrogen atom per molecule, present in 300 moles of the mesitylene would be sufficient to reduce the value of S/S_0 to 0.8. This amount of impurity could easily have been present in the mesitylene used.

Discussion

The lack of exchange of tritium between TCl and toluene is in agreement with Brown's formulation of the interaction between HCl and aromatic hydrocarbons as involving weak π-complexes[5] and indicates that there is no accessible reaction path for formation of the σ-complex in the absence of a catalyst, even at 140°. The occurrence of exchange in the presence of $SnCl_4$ shows that there is some interaction between $SnCl_4$, TCl and toluene involving the formation of a carbon–tritium bond. This occurs in a homogeneous toluene solution, unlike the common Friedel–Crafts reactions which take place in the presence of a red oil phase which is presumed to favor reaction by an ionic mechanism because of its high dielectric constant. The exchange is not a high energy process since the activation energy is low. It has a very low steric factor or, equivalently, a large negative entropy of activation. This is probably what should be expected for an activated complex similar to the σ-complexes formulated by Brown[5,6] involving a considerable separation of charge, since such complexes may require a favorable orientation of the surrounding solvent molecules for their formation.

The spectrum of $SnCl_4$ in toluene indicates the formation of a complex between these two materials. Such a complex has been proposed by de Carli[23] on the basis of viscosity measurements, and solid complexes of $SnCl_4$ with some aromatic hydrocarbons have been observed.[24] The spectra of $SnCl_4$–HCl–$C_6H_5CH_3$ systems differ from those with $AlBr_3$–HBr–$C_6H_5CH_3$[25] in that no new peaks are observed on adding the hydrogen halide although rapid exchange of chlorine is known to occur between HCl and solid, liquid or gaseous $SnCl_4$.[26] There must be some interaction in the system $SnCl_4$–HCl–$C_6H_5CH_3$ to account for the tritium exchange, but any ternary complex either does not exist in appreciable concentration or does not give appreciable absorption above 3600 Å.

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MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF ANATOMY, SCHOOL OF MEDICINE, UNIVERSITY OF WASHINGTON]

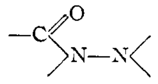
The Crystal Structure of *n*-Dodecanoic Acid Hydrazide

BY L. H. JENSEN

RECEIVED JANUARY 16, 1956

The crystal structure of *n*-dodecanoic acid hydrazide has been determined by two-dimensional projections. The structure consists of molecular ribbons held together by hydrogen bonds. These ribbons laid face-to-face make up the "molecular double layers" which are similar to those occurring in many long-chain compounds. Individual atom anisotropic temperature factor parameters have been determined for the projection on (010). They indicate electronic anisotropy of the chain atoms which corresponds to the direction of maximum thermal motion in projection essentially at right angles to the chain axis. Hydrogen atom positions have been determined and their precision indicated. Within the limit of experimental error, the chain is found to be planar and the C–C bonds, excepting those at the ends of the chain, of equal length.

A number of monoacyl derivatives of hydrazine are known to possess tuberculostatic activity. For these compounds it becomes a matter of some importance to know the exact stereochemistry of the molecule, in particular the precise configuration of



Kyame, Fisher and Bickford have shown that the monosubstituted hydrazides are satisfactory derivatives for identifying some n-aliphatic acids.[1] A plot of the melting point of derivative *vs.* number of carbon atoms in chain gives a smooth curve, *i.e.*, compounds with either an even or odd number of carbon atoms in the chain have melting points falling on the same curve. We are interested in the hydrocarbon chain packing that gives rise to this interesting observation.[2] Further, since there is evidence that "molecular double layers" occur in biological membrane systems, a better understanding of the solid state structure of long-chain polar compounds is desirable.

Experimental

Weissenberg and oscillation photographs about the b axis led to the following unit cell parameters: a_0 = 7.46 Å., b_0 = 4.88 Å., c_0 = 74.04 Å., β = 91° 2′ (Cu Kα = 1.5418 Å.). The accuracy of the linear parameters is estimated as ±0.3%.

The space group is either Aa or A2/a. With 8 molecules in the unit cell, A2/a is probable and, since this was confirmed for n-heptanoic acid hydrazide by a modification of Wilson's ratio test,[3] it was assumed for n-dodecanoic acid hydrazide. The calculated density is 1.056 g. cm.$^{-3}$.

The compound was prepared according to the method of Sah as outlined by Kyame, Fisher and Bickford.[1] Some difficulty was experienced in growing good single crystals. Similar difficulties have arisen in attempts to grow crystals of several other paraffin chain compounds. However, upon slow evaporation of a solution of the hydrazide in 95% ethanol, crystals were obtained as masses of thin plates with occasional larger specimens encrusted with micro-crystalline powder. A usable crystal was prepared by trimming away extraneous material from such a single crystal and cutting it to appropriate size and shape with a regular histological microtome fitted with a razor blade. An octagonal cylinder about 0.14 mm. across and 0.6 mm. long, [010] essentially coincident with the cylinder axis, was cut and used for collecting zero and upper level Weissenberg data.

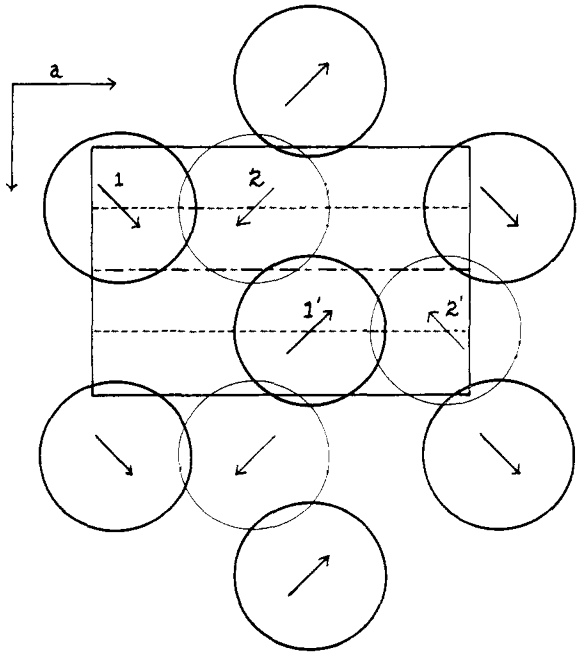


Fig. 1.—Packing of hydrogen atoms between molecular double layers. Heavy circles represent hydrogen atoms on bottom face of a double layer; light circles, those on top face of adjacent double layer. Arrow indicates orientation of carbon chain of corresponding molecule.

Integrated Weissenberg photographs[4] were taken with the camera set to integrate only along the film coördinate at right angles to the rotation axis. Optical densities were measured with a recording microphotometer by scanning along the film coördinate at right angles to the direction of integration by the camera.[5] Integrated intensities were taken as proportional to the area under the curve of optical density *vs.* film coördinate. Some of the weakest reflections were photometered on an unintegrated photograph, peak heights being assumed proportional to intensities. In this way, 248 (71%) of the 349 accessible $h0l$ reflections and 88 (62%) of the 143 usable $0kl$ reflections were measured.

The procedure outlined here has two advantages over the more usual integration along both film coördinates on the camera; the exposures are much shorter and troublesome overlap of spots for structures with one long axis can be avoided.

In order to take full advantage of the greater precision inherent in photometry, care was exercised in every phase of the experimental work. Thus the crystal was of uniform cross-section, it was accurately centered, extinction was minimized and X-ray intensity over the beam area was essentially uniform.

Crystal Disorder.—Some crystals of the shorter n-paraffin chain hydrazides give a diffraction pattern indicating a disordered structure. The disordering is pronounced for n-dodecanoic acid hydrazide. Upper level Weissenberg photographs about the b-axis showed streaking in the c^*-direction of all hkl reflections for $h + k$ odd. Since an a-axis zero level Weissenberg also showed streaking of spots in the c^*-direction for reflections with odd k, it is clear that the reciprocal lattice "points" showing the disorder are in reality rod-like in shape. The structure as deduced (see below) consists of sheet-like "molecular double layers" perpendicular to c^*. These layers must not all conform in structure or stacking to the requirements of the space group. The resulting sheet crystallites would produce particle size broadening of reflections in the c^*-direction. Further, a periodic recurrence of stacking faults would give satellites to the reflections; random faults would give streaking, again in the c^*-direction.[6,7]

In Fig. 1 is shown the packing of the terminal hydrogen atoms, H_1, of adjacent molecular double layers. These hydrogen atoms tend to closest packing, an arrangement that requires positions not differing significantly from those derived from $F_o - F_c$ syntheses. This closest packed arrangement has been used in Fig. 1 with a radius of 1.52 Å., the value for contact between these hydrogen atoms. Ideally the hydrogen atoms of layer 2 are related to those of layer 1 by the operation of the 2-fold axes at $x = {}^1/_4$, $z = 0$ and $x = {}^3/_4$, $z = 0$. In this way atom 2 is related to atom 1 and atom 2′ to atom 1′. But layer 2 may be displaced by $a_0/_2 + b_0/_2$ and the same end-to-end packing would result. Reflections hkl with $h + k$ even would be unaffected while those with $h + k$ odd would show streaking if the fault occurred at random. This explanation is not meant to imply that other faults or types of disorder do not occur but seems to account satisfactorily for that most obviously present.

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(3) L. H. Jensen and E. C. Lingafelter, *Acta Cryst.*, **6**, 300 (1953).

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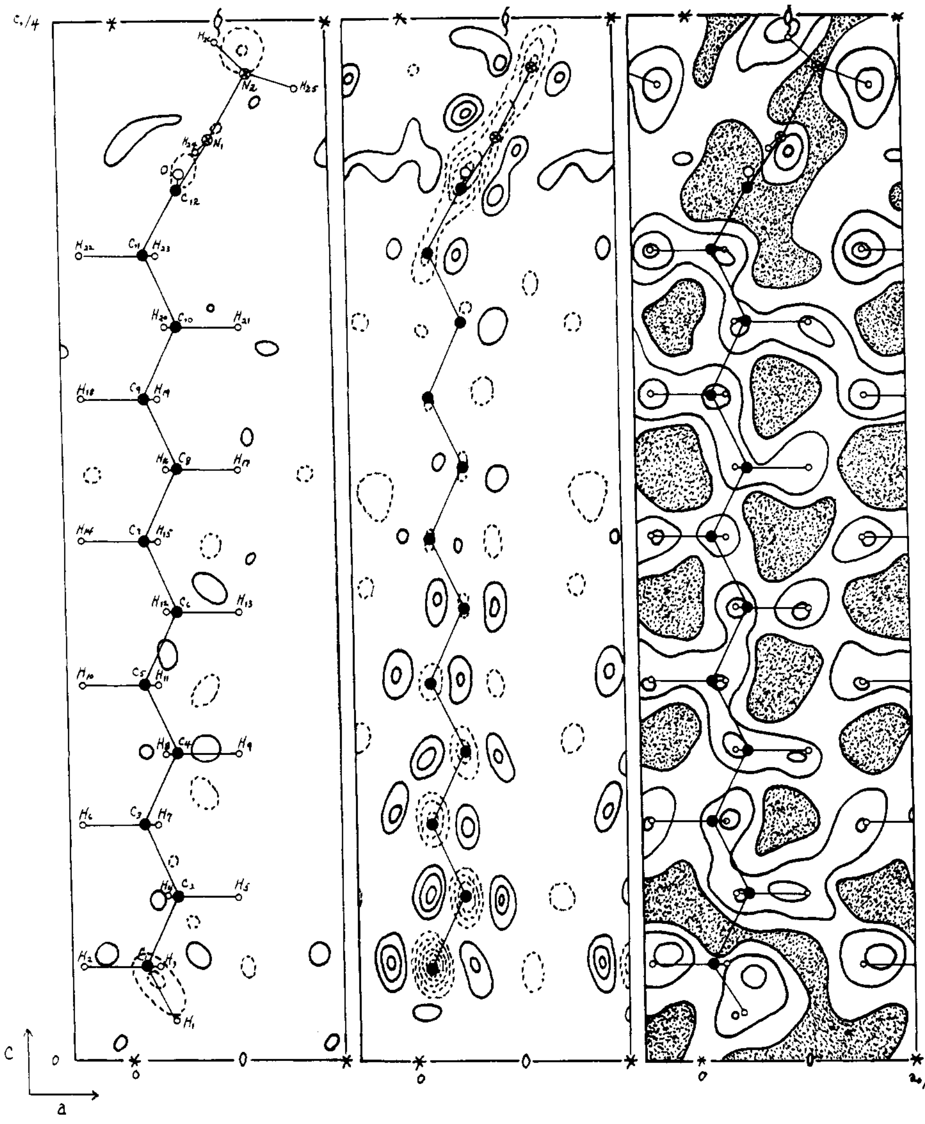

(a) (b) (c)

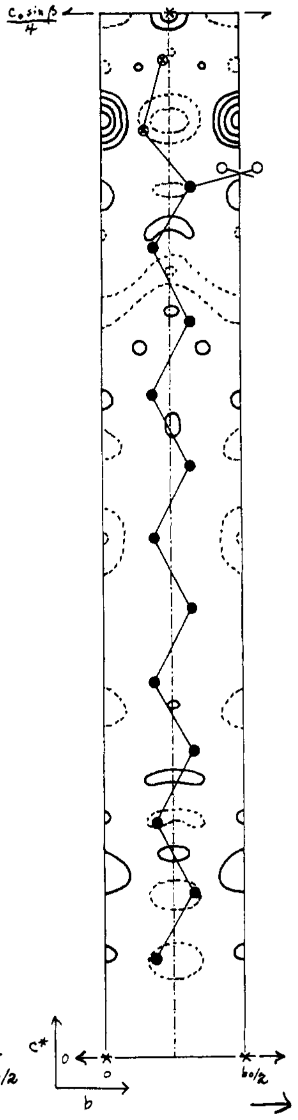

Fig. 3.

Fig. 2.—$F_0 - F_c$ syntheses on (010). Contours at intervals of 0.25 e. Å.$^{-2}$, zero contour omitted, negative contours broken: (a) final synthesis on (010), and numbering of atoms; (b) synthesis showing difference of electron density from that for spherical atoms with isotropic temperature factor, $e^{-3.0 \sin^2\theta/\lambda^2}$; (c) synthesis showing hydrogen atoms. Areas less than 0.25 e. Å.$^{-2}$ stippled.

Fig. 3.—$F_0 - F_c$ synthesis along [100]. Apparent plane of symmetry at $y = 1/4$ is a pseudo plane resulting from using only the $0kl$ data with k even. Contours at intervals of 0.125 e. Å.$^{-2}$, zero contour omitted, negative contours broken.

It has been assumed that the disordering is without major influence on the intensities of reflections not showing streaking, and these were the only ones used in the structure determination. Thus approximately half of the $0kl$ data were eliminated, and the y coördinates are rendered less accurate.

Determination of Structure.—A trial structure for *n*-dodecanoic acid hydrazide projected on (010) was based on a reasonable extrapolation from the structure for *n*-octanoic acid hydrazide[3] and was refined by $F_o - F_c$ syntheses.[8] The sixth and final difference map based on F_c's using the temperature factor parameters of Table I is shown in Fig. 2a. The numbering of the atoms is also indicated in this figure. Figure 2b shows the difference between thermal motion plus any inherent electronic anisotropy and that corresponding to a temperature

TABLE I

FINAL TEMPERATURE FACTORS, EXP-[$(B + C\cos^2\phi)\sin^2\theta/\lambda^2$] FOR F_{h0l}[a]

Atom	B(Å.)	C(Å.)	Atom	B(Å.)	C(Å.)
C_1	5.3	2.2	C_9	2.8	0.8
C_2	4.1	2.4	C_{10}	2.8	0.7
C_3	3.5	2.3	C_{11}	2.8	0.9
C_4	3.1	2.3	C_{12}	2.8	1.3
C_5	2.9	2.1	O	3.1	1.6
C_6	2.8	1.7	N_1	2.4	2.1
C_7	2.8	1.2	N_2	2.5	2.0
C_8	2.8	0.9			

[a] ϕ = angle between plane normal and direction of maximum vibration.

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(8) W. Cochran, *Acta Cryst.*, 4, 408 (1951).

[p. 3996] Table II: Observed and Calculated Structure Factors

Index	F_o	F_c
0 0 6	55.0	−52.8
0 0 8	63.0	−61.4
0,0,10	14.8	14.0
0,0,12	102.2	−104.0
0,0,14	44.4	44.6
0,0,16	98.2	−95.8
0,0,18	30.8	23.8
0,0,20	44.6	−49.2
0,0,22	21.6	−20.8
0,0,24	<3.6	4.0
0,0,26	51.6	50.8
0,0,28	21.4	23.0
0,0,30	41.0	−41.2
0,0,32	5.0	6.2
0,0,34	8.6	−6.2
0,0,36	23.2	−22.2
0,0,38	32.4	30.8
0,0,40	39.8	−43.8
0,0,42	51.0	48.6
0,0,44	38.0	−38.8
0,0,46	46.8	45.0
0,0,48	22.0	−19.2
0,0,50	25.6	28.4
0,0,52	11.6	10.6
0,0,54	13.2	12.2
0,0,56	90.6	88.2
0,0,58	<6.8	−0.4
0,0,60	104.2	−104.2
0,0,62	<6.8	2.2
0,0,64	16.4	−10.8
0,0,66	10.8	−5.8
0,0,68	8.2	9.8
0,0,70	15.0	−13.8
0,0,72	17.0	17.2
0,0,74	16.4	−16.0
0,0,76	14.8	15.0
0,0,78	13.8	−12.2
0,0,80	8.2	10.2
0,0,82	9.6	−5.2
0,0,84	<5.6	2.6
0,0,86	<5.2	0.6
0,0,88	<4.6	−1.2
0,0,90	5.1	3.2
0,0,92	<4.0	1.4
0,0,94	5.0	2.8
0 2 0	180.3	−209.6
0 2 2	6.8	4.1
0 2 4	24.7	20.2
0 2 6	10.4	10.3
0 2 8	4.3	−2.5
0,2,10	27.5	28.9
0,2,12	22.5	−19.5
0,2,14	34.0	34.2
0,2,16	22.4	−16.9
0,2,18	22.4	18.3
0,2,20	<4.4	5.3
0,2,22	<4.6	−5.7
0,2,24	23.1	26.6
0,2,26	22.1	−22.9
0,2,28	32.7	33.2
0,2,30	20.9	−22.5
0,2,32	21.7	20.9
0,2,34	11.1	−8.6
0,2,36	7.7	7.2
0,2,38	6.5	1.2
0,2,40	<6.6	1.2
0,2,42	8.9	−2.6
0,2,44	7.8	3.8
0,2,46	14.5	−13.8
0,2,48	11.9	12.8
0,2,50	17.1	−20.1
0,2,52	<7.8	11.3
0,2,54	17.0	−18.9
0,2,56	32.2	−27.7
0,2,58	<8.2	−10.3
0,2,60	47.3	54.6
0,2,62	<8.2	−1.3
0,2,64	<8.2	−1.7
0,2,66	11.7	11.9
0,2,68	10.4	−15.3
0,2,70	14.1	15.6
0,2,72	11.4	−14.8
0,2,74	<7.4	10.2
0,2,76	<7.2	−6.7
0,2,78	<6.9	2.9
0,2,80	<6.5	−0.8
0,2,82	<6.1	−1.4
0,2,84	<5.6	1.4
0,2,86	<5.1	−0.8
0,2,88	<4.4	−1.4
0 4 0	5.0	−0.1
0 4 2	3.3	1.3
0 4 4	4.2	0.1
0 4 6	<1.7	−1.4
0 4 8	<2.0	4.0
0,4,10	5.6	−6.0
0,4,12	7.9	10.3
0,4,14	9.8	−10.7
0,4,16	10.4	10.6
0,4,18	8.9	−8.7
0,4,20	6.2	5.0
0,4,22	3.6	−1.6
0,4,24	3.4	−2.5
0,4,26	6.2	6.0
0,4,28	9.0	−8.9
0,4,30	7.5	8.3
0,4,32	6.8	−7.1
0,4,34	5.1	6.6
0,4,36	4.9	7.2
0,4,38	6.3	5.9
0,4,40	4.9	6.4
0,4,42	4.9	6.3
0,4,44	<4.1	−5.6
0,4,46	<4.1	5.4
0,4,48	<4.1	−4.3
0,4,50	<4.1	1.4
0,4,52	<4.0	−0.8
0,4,54	<4.0	−1.3
0,4,56	<3.9	0.5
0,4,58	<3.8	−1.2
0,4,60	<3.7	2.7
0,4,62	<3.5	−0.3
0,4,64	<3.3	0.3
0,4,66	<3.1	0.2
0,4,68	<2.9	−0.2
2 0 0	75.2	71.8
2 0 2	126.2	−128.0
2 0 4	63.4	−62.8
2 0 6	31.8	−29.6
2 0 8	18.8	−18.8
2,0,10	22.6	−24.4
2,0,12	4.6	−2.8
2,0,14	4.8	−5.6
2,0,16	15.0	−17.0
2,0,18	22.4	25.2
2,0,20	33.0	−38.8
2,0,22	43.8	45.6
2,0,24	45.6	−49.4
2,0,26	65.6	61.2
2,0,28	165.6	160.8
2,0,30·	55.8	−49.8
2,0,32	58.4	54.0
2,0,34	14.0	−13.0
2,0,36	40.8	37.4
2,0,38	6.4	−6.6
2,0,40	25.8	22.4
2,0,42	<5.6	4.6
2,0,44	14.4	12.2
2,0,46	10.6	9.0
2,0,48	15.4	12.0
2,0,50	8.2	5.6
2,0,52	21.6	18.8
2,0,54	<6.6	3.6
2,0,56	47.8	50.4
2,0,58	106.4	−103.0
2,0,60	11.0	−6.8
2,0,62	<6.8	4.8
2,0,64	<7.0	2.6
2,0,66	<7.6	8.2
2,0,68	5.2	−4.2
2,0,70	12.6	10.2
2,0,72	11.0	−8.0
2,0,74	10.8	8.2
2,0,76	9.8	−7.4
2,0,78	6.6	5.4
2,0,80	6.4	−4.8
2,0,82	<5.6	1.2
2,0,84	8.8	−9.2
2,0,86	13.8	−10.6
2,0,88	28.8	23.0
2,0,90	6.0	3.8
2,0,92	<3.0	2.2
4 0 0	71.4	−67.8
4 0 2	42.8	−38.6
4 0 4	18.4	−16.0
4 0 6	11.8	6.2
4 0 8	12.0	−14.1
4,0,10	7.8	3.0
4,0,12	6.0	4.2
4,0,14	12.8	−17.2
4,0,16	24.0	25.2
4,0,18	29.6	−33.8
4,0,20	33.0	32.4
4,0,22	40.0	−42.0
4,0,24	33.4	32.4
4,0,26	60.2	−58.6
4,0,28	71.8	−71.6
4,0,30	53.8	52.0
4,0,32	45.6	44.2
4,0,34	11.4	−10.8
4,0,36	35.2	37.0
4,0,38	21.8	−19.2
4,0,40	24.8	27.2
4,0,42	14.2	−11.0
4,0,44	9.4	9.4
4,0,46	9.6	6.6
4,0,48	14.4	−10.8
4,0,50	23.0	22.4
4,0,52	27.2	−26.4
4,0,54	38.0	36.2
4,0,56	45.6	−45.0
4,0,58	12.4	−11.8
4,0,60	6.8	4.8
4,0,62	8.6	9.8
4,0,64	<6.6	0.8
4,0,66	<6.4	−0.4
4,0,68	<6.2	4.0
4,0,70	6.0	−5.0
4,0,72	<5.8	2.6
4,0,74	<5.6	−2.8
4,0,76	<5.2	−1.6
4,0,78	<4.8	2.0
4,0,80	8.6	−7.6
4,0,82	6.2	5.4
4,0,84	21.0	−21.6
6 0 0	<6.6	7.0
6 0 2	11.4	−14.6
6 0 4	11.8	9.8
6 0 6	<6.6	−4.4
6 0 8	<6.6	−2.6
6,0,10	6.4	4.6
6,0,12	8.0	−10.0
6,0,14	8.6	7.8
6,0,16	8.6	−10.1
6,0,18	6.4	1.8
6,0,20	7.6	−8.2
6,0,22	5.2	−4.6
6,0,24	<6.8	−1.0
6,0,26	52.0	−48.6
6,0,28	7.8	10.4
6,0,30	67.8	73.8
6,0,32	30.0	−25.8
6,0,34	25.6	26.0
6,0,36	16.0	−17.4
6,0,38	9.2	12.0
6,0,40	6.4	−6.8
6,0,42	<6.8	0.2
6,0,44	8.2	3.8
6,0,46	9.6	8.6
6,0,48	9.6	9.2
6,0,50	10.4	−11.6
6,0,52	11.0	9.2
6,0,54	8.0	−8.4
6,0,56	<6.0	0.6
6,0,58	<5.6	0.0
6,0,60	<5.4	−2.8
6,0,62	<5.2	4.8
6,0,64	6.6	−6.6
6,0,66	4.8	4.4
6,0,68	<4.2	−3.2
6,0,70	<3.8	−1.0
6,0,72	<3.2	3.0
8 0 0	<6.2	−0.2
8 0 2	9.2	−10.2
8 0 4	<6.2	2.2
8 0 6	<6.2	−3.2
8 0 8	<6.2	−2.8
8,0,10	<6.2	0.0
8,0,12	6.2	−7.6
8,0,14	8.4	7.8
8,0,16	10.2	−10.8
8,0,18	9.0	6.4
8,0,20	9.2	−9.0
8,0,22	7.2	6.0
8,0,24	9.2	−8.2
8,0,26	19.6	−12.8
8,0,28	36.6	39.2
8,0,30	<5.4	−7.8
8,0,32	<5.2	1.0
8,0,34	<5.2	−5.8
8,0,36	<5.0	3.0
8,0,38	<4.8	−3.4
8,0,40	<4.6	0.4
8,0,42	<4.4	0.6
8,0,44	5.4	−2.4
8,0,46	<3.8	2.8
8,0,48	<3.4	−2.2
2 0 $\bar{2}$	362.0	414.2
2 0 $\bar{4}$	135.4	−142.0
2 0 $\bar{6}$	147.6	158.6
2 0 $\bar{8}$	63.8	−64.0
2,0,$\overline{10}$	31.0	31.8
2,0,$\overline{12}$	30.8	31.8
2,0,$\overline{14}$	75.4	−81.2
2,0,$\overline{16}$	99.0	103.2
2,0,$\overline{18}$	127.4	−136.2
2,0,$\overline{20}$	104.4	108.0
2,0,$\overline{22}$	119.8	−124.6
2,0,$\overline{24}$	45.2	45.0
2,0,$\overline{26}$	72.4	−70.8
2,0,$\overline{28}$	116.8	−118.4
2,0,$\overline{30}$	77.0	70.4
2,0,$\overline{32}$	47.8	41.2
2,0,$\overline{34}$	17.0	17.4
2,0,$\overline{36}$	8.0	−7.4
2,0,$\overline{38}$	8.4	7.0
2,0,$\overline{40}$	14.6	−14.6
2,0,$\overline{42}$	<5.4	−0.4
2,0,$\overline{44}$	16.2	16.0
2,0,$\overline{46}$	26.6	−24.0
2,0,$\overline{48}$	24.4	24.0
2,0,$\overline{50}$	27.2	−24.8
2,0,$\overline{52}$	21.0	21.8
2,0,$\overline{54}$	10.8	−15.2
2,0,$\overline{56}$	31.2	28.4
2,0,$\overline{58}$	80.6	78.4
2,0,$\overline{60}$	44.0	−39.4
2,0,$\overline{62}$	25.8	−23.4
2,0,$\overline{64}$	8.0	−6.8
2,0,$\overline{66}$	15.0	−6.8
2,0,$\overline{68}$	7.6	−5.6
2,0,$\overline{70}$	<6.8	−3.0
2,0,$\overline{72}$	8.2	−8.4
2,0,$\overline{74}$	<6.6	6.4
2,0,$\overline{76}$	13.2	−11.4
2,0,$\overline{78}$	10.8	8.4
2,0,$\overline{80}$	15.2	−12.2
2,0,$\overline{82}$	12.0	9.0
2,0,$\overline{84}$	15.4	−13.4
2,0,$\overline{86}$	12.0	11.2
2,0,$\overline{88}$	20.4	19.4
2,0,$\overline{90}$	10.4	−9.8
2,0,$\overline{92}$	<3.4	−0.6
4 0 $\bar{2}$	71.4	64.6
4 0 $\bar{4}$	59.4	61.0
4 0 $\bar{6}$	37.0	−30.8
4 0 $\bar{8}$	59.2	61.0
4,0,$\overline{10}$	36.8	−30.0
4,0,$\overline{12}$	33.6	36.8
4,0,$\overline{14}$	<5.2	−0.2
4,0,$\overline{16}$	10.4	−8.2
4,0,$\overline{18}$	38.4	40.8
4,0,$\overline{20}$	45.8	−47.6
4,0,$\overline{22}$	64.8	65.4
4,0,$\overline{24}$	63.4	−68.4
4,0,$\overline{26}$	71.2	67.6
4,0,$\overline{28}$	96.2	−103.8
4,0,$\overline{30}$	57.4	−54.6
4,0,$\overline{32}$	60.2	59.2
4,0,$\overline{34}$	10.8	−5.8
4,0,$\overline{36}$	27.6	24.0
4,0,$\overline{38}$	14.2	−11.6
4,0,$\overline{40}$	18.4	17.2
4,0,$\overline{42}$	9.2	−8.2
4,0,$\overline{44}$	7.6	3.4
4,0,$\overline{46}$	<6.6	0.0
4,0,$\overline{48}$	7.2	−4.2
4,0,$\overline{50}$	<6.8	4.4
4,0,$\overline{52}$	11.6	−7.6
4,0,$\overline{54}$	<7.0	2.0
4,0,$\overline{56}$	10.4	−12.4
4,0,$\overline{58}$	23.2	26.2
4,0,$\overline{60}$	29.0	26.8
4,0,$\overline{62}$	21.6	−22.2
4,0,$\overline{64}$	13.4	8.8
4,0,$\overline{66}$	14.2	−12.0
4,0,$\overline{68}$	<6.4	6.4
4,0,$\overline{70}$	<6.2	−7.6
4,0,$\overline{72}$	<6.0	1.8
4,0,$\overline{74}$	<5.8	−3.4
4,0,$\overline{76}$	<5.4	−1.0
4,0,$\overline{78}$	<5.2	−0.6
4,0,$\overline{80}$	<4.8	−4.2
4,0,$\overline{82}$	<4.4	−0.4
4,0,$\overline{84}$	8.2	−6.6
4,0,$\overline{86}$	13.6	−14.2
6 0 $\bar{2}$	14.8	−17.0
6 0 $\bar{4}$	21.4	16.2
6 0 $\bar{6}$	<6.6	−4.8
6 0 $\bar{8}$	<6.6	4.6
6,0,$\overline{10}$	<6.6	3.2
6,0,$\overline{12}$	<6.6	−0.8
6,0,$\overline{14}$	6.6	7.8
6,0,$\overline{16}$	<6.8	0.4
6,0,$\overline{18}$	<6.8	4.6
6,0,$\overline{20}$	7.6	7.0
6,0,$\overline{22}$	<6.8	0.8
6,0,$\overline{24}$	18.0	13.0
6,0,$\overline{26}$	<6.8	1.4
6,0,$\overline{28}$	31.8	29.8
6,0,$\overline{30}$	78.4	−84.0
6,0,$\overline{32}$	<7.0	−5.4
6,0,$\overline{34}$	24.4	23.6
6,0,$\overline{36}$	17.4	−16.4
6,0,$\overline{38}$	20.0	21.0
6,0,$\overline{40}$	14.4	−16.4
6,0,$\overline{42}$	20.8	19.6
6,0,$\overline{44}$	12.0	−12.6
6,0,$\overline{46}$	9.2	9.6
6,0,$\overline{48}$	<6.6	−4.0
6,0,$\overline{50}$	<6.6	1.6
6,0,$\overline{52}$	<6.4	3.4
6,0,$\overline{54}$	<6.2	−3.8
6,0,$\overline{56}$	<5.8	3.4
6,0,$\overline{58}$	<5.8	−1.8
6,0,$\overline{60}$	<5.8	3.0
6,0,$\overline{62}$	<5.4	2.2
6,0,$\overline{64}$	<5.2	−1.4
6,0,$\overline{66}$	<4.8	3.0
6,0,$\overline{68}$	<4.6	−3.2
6,0,$\overline{70}$	<4.2	4.8
6,0,$\overline{72}$	<3.8	−4.0
6,0,$\overline{74}$	<3.2	3.4
8 0 $\bar{2}$	19.2	23.0
8 0 $\bar{4}$	12.4	−10.6
8 0 $\bar{6}$	<6.2	2.8
8 0 $\bar{8}$	<6.2	−2.0
8,0,$\overline{10}$	<6.2	0.8
8,0,$\overline{12}$	<6.2	−1.2
8,0,$\overline{14}$	<6.2	−0.8
8,0,$\overline{16}$	<6.2	1.2
8,0,$\overline{18}$	<6.0	−0.6
8,0,$\overline{20}$	<6.0	1.0
8,0,$\overline{22}$	<6.0	0.8
8,0,$\overline{24}$	<5.8	1.6
8,0,$\overline{26}$	<5.8	−0.2
8,0,$\overline{28}$	21.6	18.8
8,0,$\overline{30}$	<5.6	−3.2
8,0,$\overline{32}$	25.8	27.6
8,0,$\overline{34}$	<5.2	8.0
8,0,$\overline{36}$	<5.2	0.0
8,0,$\overline{38}$	<5.0	−4.6
8,0,$\overline{40}$	4.4	6.2
8,0,$\overline{42}$	5.2	−8.0
8,0,$\overline{44}$	6.6	9.6
8,0,$\overline{46}$	5.0	−9.2
8,0,$\overline{48}$	3.6	7.8
8,0,$\overline{50}$	<3.6	−6.0
8,0,$\overline{52}$	<3.2	4.2

factor $e^{-3.0 \sin^2 \theta/\lambda^2}$. It is clear from the difference map that in regard to direction of maximum vibration the atoms fall essentially into two groups. The direction of maximum vibration in projection was taken as −4° from the *a*-axis for C_{1-11} and −22° for C_{12}, O, N_1 and N_2.

Figure 2c is a difference map showing the H atoms. H_{4-23} may be placed rather accurately by stereochemical considerations coupled with the spectroscopic C–H bond length. From the positions thus determined of these 20 hydrogen atoms, the standard deviation of the peaks is 0.15 Å. The range of peak heights for all 26 H's is 0.7 − 1.0 e. Å.$^{-2}$ with an average of 0.8 e. Å.$^{-2}$. For data collected at liquid nitrogen temperature, a peak height of 2.2 e. Å.$^{-2}$ may be expected.[9] Hence, using photometric integrated data collected from a crystal at that temperature, one would expect a standard deviation of only about 0.05 Å. in projected H atom positions.

A plot of electron density projected on (010) was made. Although the one electron contour indicated many of the H atoms and peak heights and shapes allowed rough estimates of temperature factor parameters, comparison with Figs. 2b and 2c indicated how much more powerful $F_o - F_c$ syntheses are for these purposes. Furthermore $F_o - F_c$ syntheses greatly reduce series termination error.

For final F_{h0l}, $R = 8.1\%$; neglecting H atoms, $R = 11.6\%$; using over-all isotropic temperature factor $e^{-3.0 \sin^2 \theta/\lambda^2}$, $R = 14.6\%$; using this same temperature factor and neglecting H atoms, $R = 16.7\%$, based on F_c's scaled by the least squares factor, $f = \Sigma_{\text{obsd}} |F_r| |F_c| / \Sigma_{\text{obsd}} |F_r|^2$. All values of *R* quoted in this paper are based on F_o's only and omit $F_{20\bar{2}}$ and F_{020} which are low due to extinction.

The approximate structure of *n*-nonanoic acid hydrazide projected along [100][3] was the basis for a satisfactory trial structure for the corresponding projection of *n*-dodecanoic acid hydrazide. Refinement proceeded by $F_o - F_c$ syntheses. For the sixth and final $F_o - F_c$ map, Fig. 3, *F*'s included individual anisotropic temperature factors derivable from the *h*0*l* parameters by assuming vibration amplitude in the *b* direction to be approximately identical with the maximum in projection on (010). For the final F_{0kl}, $R = 9.5\%$ using individual level scale factors.

The structure based only on F_{h0l} and F_{0kl} is not unique since a translation of $a_0/4$ results in a structure with identical $|F_c|$. The position reported here was confirmed by calculating $F_{1,1,29}$ and $F_{1,1,1,31}$ for the two possibilities.

Observed structure factors, F_o, and final F_c are listed in Table II. From the parameters of Table III, the bond lengths and angles of Table IV were calculated.

Treatment of Data and Accuracy of Results.—In the early stages of refining a structure, considerable numbers of the smallest *F*'s may be of questionable phase. There is some advantage in omitting from the difference synthesis the ΔF's for such reflections. A 50% rule, *i.e.*, omitting ΔF if $F_c < F_o/2$, is useful in eliminating most of the reflections which subsequently change sign. The omitted terms which are of correct sign decrease somewhat the calculated shifts but may be allowed

TABLE III

ATOMIC PARAMETERS

	x/a_0	y/b_0	z/c_0
C_1	0.0349	0.1823	0.0220
C_2	.1192	.3181	.0395
C_3	.0381	.1819	.0565
C_4	.1229	.3156	.0736
C_5	.0425	.1856	.0907
C_6	.1264	.3162	.1080
C_7	.0475	.1848	.1251
C_8	.1340	.3170	.1422
C_9	.0534	.1860	.1595
C_{10}	.1410	.3146	.1766
C_{11}	.0568	.1922	.1938
C_{12}	.1472	.3251	.2096
O	.1546	.5671	.2133
N_1	.2221	.1593	.2219
N_2	.3123	.2218	.2380
H_1	.095	.279	.0116
H_2	.891	.224	.0216
H_3	.062	.961	.0216
H_4	.094	.542	.0394
H_5	.264	.279	.0394
H_6	.893	.224	.0566
H_7	.063	.961	.0566
H_8	.097	.542	.0736
H_9	.267	.279	.0736
H_{10}	.898	.224	.0907
H_{11}	.068	.961	.0907
H_{12}	.101	.542	.1078
H_{13}	.271	.279	.1078
H_{14}	.903	.224	.1252
H_{15}	.074	.961	.1252
H_{16}	.109	.542	.1422
H_{17}	.279	.279	.1422
H_{18}	.909	.224	.1596
H_{19}	.079	.961	.1596
H_{20}	.115	.542	.1768
H_{21}	.286	.279	.1768
H_{22}	.912	.224	.1939
H_{23}	.082	.961	.1939
H_{24}	.216	.965	.2178
H_{25}	.432	.316	.2336
H_{26}	.249	.400	.2440

TABLE IV

BOND LENGTHS AND BOND ANGLES

	Length, Å.		Angle, degree
C_1-C_2	1.576	$C_1-C_2-C_3$	109.4
C_2-C_3	1.554	$C_2-C_3-C_4$	108.9
C_3-C_4	1.549	$C_3-C_4-C_5$	109.8
C_4-C_5	1.546	$C_4-C_5-C_6$	110.6
C_5-C_6	1.551	$C_5-C_6-C_7$	110.6
C_6-C_7	1.545	$C_6-C_7-C_8$	109.7
C_7-C_8	1.551	$C_7-C_8-C_9$	109.8
C_8-C_9	1.560	$C_8-C_9-C_{10}$	110.0
C_9-C_{10}	1.544	$C_9-C_{10}-C_{11}$	110.2
$C_{10}-C_{11}$	1.549	$C_{10}-C_{11}-C_{12}$	107.1
$C_{11}-C_{12}$	1.488	$C_{11}-C_{12}-O$	128.2
$C_{12}-O$	1.211	$C_{11}-C_{12}-N_1$	116.9
$C_{12}-N_1$	1.332	$C_{12}-N_1-N_2$	130.0
N_1-N_2	1.392	$O-C_{12}-N_1$	114.8
$N_1-H_{24}—O'$	3.00	$N_1-H_{24}-O'$	163.6
$N_2-H_{26}—N_2''$	3.17	$N_2-H_{26}-N_2''$	163.4

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(9) F. L. Hirshfeld and G. M. J. Schmidt, *Acta Cryst.*, **7**, 192 (1954).

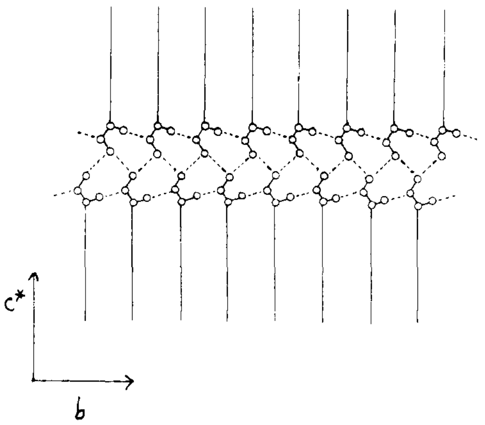

Fig. 4.—Schematic molecular ribbon showing hydrogen bonding.

for roughly by dividing by the fraction of the terms used.

In this work those unobserved reflections were included in the difference synthesis for which F_c was greater than the minimum observed value, F_{min}, and ΔF was taken as $F_{\text{min}} - F_c$. It has been suggested that in least squares treatment of the data all unobserved F's should be included and taken equal to their mean value with weighting inversely proportional to the variance, σ^2.[10] Now although the least squares method and difference syntheses are fundamentally related,[11] it is not advisable to treat unobserved F's in this way in difference syntheses since weighting of ΔF's by a factor other than 1 precludes a direct interpretation of the difference map in terms of electron densities. Unless exposures are rather long or the crystal quite large, the mean value of the unobserved F's considerably exceeds σ and appreciable errors could result by including these terms without weighting.

From the 50 observed $F_{02l,\,04l}$, 17 parameters are determined: 15 y coördinates and 2 level factors. There are only $2.9F_0$ per parameter, an unsatisfactorily low value. However, since quite long exposures were taken, the average minimum value of the F_o's is $\sim 0.5\%$ of the 960 electrons in the unit cell. Hence, the unobserved F's may quite legitimately be considered as observables with a larger error. Even then there are only 4.9 "observables" per parameter.

For the structure projected on (010), 63 parameters were determined: 30 positional, 32 temperature factor and one scale constant from a total of the 349 observed plus unobserved F's. These figures emphasize the need for care in interpreting results of two-dimensional work when individual atom anisotropic temperature factor parameters have been introduced.

Standard deviations of position were calculated for C atoms by applying Cruickshank's equations to $F_o - F_c$.[12] $F_{20\bar{2}}$ and F_{020} were neglected because of extinction effects. One calculates

$$\sigma(A_h) = 0.430,\ \sigma(A_k) = 0.528,\ \sigma(A_l) = 0.440$$

where the values have been multiplied by $[u/(u - v)]^{1/2}$[13] and $\sigma(A_k)$ has also been multiplied by $\sqrt{2}$ to allow for the contribution of the unusable $0kl$ data. Since the electron density, ρ, of some of the atoms is quite anisotropic, the standard deviation in position will vary appreciably with direction. Neglecting this we may reasonably set

$$\partial^2\rho/\partial x^2 = \partial^2\rho/\partial y^2 = \partial^2\rho/\partial z = 50 \text{ e. Å.}^{-3}$$

for C atoms in the chain. This gives

$$\sigma_x = 0.0086 \text{ Å.},\ \sigma_y = 0.0106 \text{ Å.},\ \sigma_z = 0.0088 \text{ Å.}$$

with r.m.s. of 0.0094 Å. and $\sigma_{C-C} = 0.013$ Å.

Machine Calculations.—During the course of the work reported here, an I.B.M. type 604 electronic calculating punch became available. All F_c's beyond the fourth refinement of the $h0l$ data and the second refinement of the $0kl$ data were machine calculated.

Sine and cosine functions for any angle were calculated to three decimal places for the related angle or its complement in the first octant, and by appropriate selectors the sign and function were chosen for the particular argument. The result was checked by squaring, adding and testing to determine that the sum of the squares was 1.000 ± 0.002.

Temperature factors were calculated using the series for e^{-x} through the eighth power of x. The results were never in error by more than 0.0005 for $(B + C) < 3.5$. The accuracy was sufficient so that for $(B + C) > 3.5$, the series for $(B + C)/2$ or $(B + C)/3$ could be calculated and the result squared or cubed and rounded to three decimal places.

The calculation of the 349 F_{h0l} for the 15 heavier atoms in the asymmetric unit of n-dodecanoic acid hydrazide required 3.5 hr. using an over-all temperature factor and 5.5 hr. using individual atom temperature factors. The time required for these same calculations using an electric desk calculator and no check was about 20 times as long. For certain other calculations, *e.g.*, $\sin^2\theta$, the advantage of automatic computing proved to be even greater.

Discussion

The ideal structure consists of infinite ribbons of molecules held together by N–H---O and N·H---N bonds, Fig. 4. These ribbons laid face-to-face build up sheets of molecules (the "molecular double layer") with the chains almost perpendicular to the plane of the sheets and in a head-to-head arrangement.

The a and b unit cell dimensions of the hydrazides are remarkably close to the $a_0 = 7.47$ Å. and $b_0 = 4.98$ Å. for the hydrocarbon $C_{29}H_{60}$.[14] The details of molecular arrangements are also remarkably similar. Both have an a glide and 2_1 parallel to b. But in the hydrocarbon successive layers of molecules are related by a net glide in (100) instead of A centering. The symmetry present in both structures is associated with close packing of the molecules both side-to-side and end-to-end.

The cutting properties of crystals with the molecular arrangement of the hydrazides would be expected to be anisotropic. When the ab face is cut,

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[10] W. C. Hamilton, *Acta Cryst.*, **8**, 185 (1955).

[11] D. W. J. Cruickshank, *ibid.*, **5**, 511 (1952).

[12] D. W. J. Cruickshank, *ibid.*, **2**, 65 (1949).

[13] D. W. J. Cruickshank, *ibid.*, **2**, 154 (1949).

[14] A. Müller, *Proc. Roy. Soc. (London)*, **A120**, 437 (1928).

thin sheets are planed off with only slight force on the blade. This corresponds to separation of sheets of molecular double layers held by the weak van der Waals forces between methyl groups. On the other hand, when cutting the *ac* face, material is cut away as a fine powder and a much greater force is required on the blade. To remove material from this face requires breaking the hydrogen bonds of the infinite molecular ribbons. The bc face has cutting properties intermediate between those of the other two and corresponds to separating molecular ribbons from the double layers.

The range in C–C bond lengths in the paraffin chain neglecting the end bonds, *i.e.*, C_1–C_2 and C_{11}–C_{12}, is 1.544–1.560 Å., average 1.550 Å. It can be shown that $\sigma_{\text{mean}} = \sigma_x({}^1/_9[8 \cdot 2^2 \cos^2 55° + 2])^{1/2} = 0.0037$ Å. Using Cruickshank's suggested criteria for assessing significance,[12] we find a probability of 0.99 that the average C–C bond length will not differ from the true value by more than ±0.0084 Å. Thus there is no significant difference between the average of the C–C bonds in this chain and the 1.544 Å. C–C bond length in diamond.

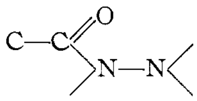
The C_1–C_2 bond is long by 0.032 Å. There is a probability of only 0.01 that a C–C bond will be in error by more than (σ_{c-c}) (2.3) = 0.030 Å. However, the C atoms at the end of the chain have temperature factor parameters considerably larger than the average, the curvature is thus smaller, σ larger. Therefore, this bond may not be significantly long. On the other hand, C_{11}–C_{12} is short and the difference between its value and that of a single bond, 0.056 Å., is highly significant. Its value is not very different from corresponding bonds adjacent to a ring.[5,15,16] In those cases conjugation results in considerable shortening of the bond. But conjugation cannot take place in the *n*-paraffin chain hydrazides. Nevertheless, C_{11}–C_{12} would be expected to be short for the reason discussed by Mulliken, Rieke and Brown.[17] The shortening should be somewhat less than that produced by conjugation. The other bonds, C_{12}–N_1, C_{12}–O and N_1–N_2 all agree within the limit of experimental error with the corresponding bonds in isonicotinic acid hydrazide.[5]

The length of the N–H---N bond is 3.17 Å. Thus it is appreciably weaker than the 2.97 and 3.04 Å. bonds of isonicotinic acid hydrazide or the 2.92 Å. bond in creatinine.[18] The N–H---O bond length is 3.00 Å., higher than the usual values for similar bonds.[19,20]

The range of the bond angles in the paraffin chain is 108.9° to 110.6° neglecting the angle nearest each end of the chain. The average is 110.0°, in satisfactory agreement with the tetrahedral angle. The standard deviation of the eight individual values is 0.5°. It is reasonable to expect a value somewhat higher than that for the tetrahedral angle, and values as high as 114° have been reported. Such deviations may be due in part to the tendency of F_o syntheses, on which most work on paraffin chain compounds has been based, to give high values for the bond angles and low values for bond lengths within the chain. Similar errors may be accentuated in two-dimensional work where overlap may become serious. However, appreciable differences among the bond angles in paraffin chains may well exist. Since the energy required to bend a bond is relatively low, packing energies should be sufficient to produce considerable deviations from ideal values.

From the value of σ for the $\angle$ C–C–C in the chain, one concludes that $\angle C_{10}$–C_{11}–C_{12} differs significantly from the tetrahedral angle but $\angle C_1$–C_2–C_3 does not and $\angle$'s C_{11}–C_{12}–N_1, C_{11}–C_{12}–O, O–C_{12}–N and C_{12}–N_1–N_2 all differ significantly from the trigonal angle, 120°, and three of them also differ significantly from corresponding angles in isonicotinic acid hydrazide.

The atoms of the chain lie close to the plane $1.5138x - 1.4846y + 0.0065z + 1 = 0$ (referred to *a*, *b* and c^* as coördinate axes) determined by least squares, neglecting C_1 and C_{12}. The mean distance of all 12 chain C's from this plane is 0.009 Å. The probability is 0.99 that if the chain is planar any particular atom will lie within (0.0094) (2.3) = 0.022 Å. of the plane. None of the chain atoms lie outside this limit. We may say, therefore, that the chain, including C_1 and C_{12}, is planar within the accuracy of this determination. The angle between the plane of the chains and the *ab* plane of the unit cell is 89.82°.

The  group is nearly planar, C_{11} and C_{12} laying + 0.08 and −0.05 Å., respectively, from the plane determined by $OC_{12}N_1$. These deviations are significant and are to be attributed to packing effects and the hydrogen bonding involving O, N_1 and N_2. The plane through $OC_{12}N$ makes an angle of 54.5° with that of the chain.

Details of the hydrocarbon chain packing will be discussed in a subsequent paper on the structure of *n*-nonanoic acid hydrazide. Although the calculations are not yet complete for that compound, it is evident that packing of the chains and the system of hydrogen bonds are essentially identical and the melting point curve of the hydrazides is satisfactorily explained.

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