

function and error program (Busing, Martin & Levy, 1962) and a much modified block-diagonal least-squares program (*World List of Crystallographic Computer Programs*, 1966).

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The Crystal Structure of Nitrilotriacetic Acid

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The crystal structure of nitrilotriacetic acid has been determined by the application of the symbolic addition technique. Three-dimensional data were collected photographically about two axes with copper $K\alpha$ radiation. The coordinates of the six methylene-hydrogen atoms and the coordinates and anisotropic temperature parameters for the thirteen heavier atoms were refined by the method of least squares. The final R index was 0.093. The molecule of nitrilotriacetic acid exists in the crystal as the zwitterion $\text{HN}^+(\text{CH}_2\text{COOH})_2\text{CH}_2\text{COO}^-$. The hydrogen atom bonded to nitrogen appears to form a bifurcated hydrogen bond. The two remaining acidic hydrogen atoms form strong hydrogen bonds of only 2.51 Å length, which connect the molecules into two interpenetrating helical networks. The crystals are monoclinic, space group Cc with $a=7.9936$, $b=18.512$, $c=6.493$ Å and $\beta=127.73^\circ$, but there exists a nearly orthogonal cell which provides a simple description of these networks. The bond distances and angles are normal within experimental error.

Introduction

Nitrilotriacetic acid is widely used in complexometric titrations, and its acid and complexometric properties have been thoroughly studied (Schwarzenbach, Kamptsch & Steiner, 1945; Schwarzenbach, Ackermann & Ruckstuhl, 1949; and Schwarzenbach & Freitag, 1951). The pK values for this molecule in 0.1*N* KCl at 20°C, as determined by Schwarzenbach and his coworkers, are:

$$\begin{aligned} pK_1 &= 1.89 \\ pK_2 &= 2.49 \\ pK_3 &= 9.73 \end{aligned}$$

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The present investigation was initiated in order to determine whether the zwitterion, $\text{HN}^+(\text{CH}_2\text{COOH})_2\text{CH}_2\text{COO}^-$, is the stable form of the molecule in the crystal.

Experimental

Small needlelike crystals were obtained by slow evaporation of an aqueous solution of nitrilotriacetic acid. A pH of 2.3 was measured for this saturated solution. Unit-cell parameters were determined from Straumanis-type single-crystal rotation photographs about the b and c axes. The resulting values for the unit-cell dimensions are given in Table 1. The absence of hkl reflections with $h+k$ odd and the absence of $h0l$ reflections with l odd indicate that the space group is either Cc or $C2/c$.

The density of the crystals as measured by the flotation method is 1.660 ± 0.003 g.cm⁻³. The density cal-

Table 1. Unit-cell dimensions for nitrilotriacetic acid

<i>a</i>	7.9936 ± 0.0001 Å
<i>b</i>	18.512 ± 0.002
<i>c</i>	6.493 ± 0.002
β	127.73° ± 0.03°
$\lambda(\text{Cu } K\alpha_1)$	1.54050 Å

culated for nitrilotriacetic acid, assuming four molecules per unit cell, is 1.671 g.cm⁻³.

Intensity data were collected for layers 0–15 about the *b* axis and 0–3 about the *c* axis from crystals of approximately 0.2 mm thickness. The multiple-film equi-inclination Weissenberg technique was used with Cu *K* α radiation. The author is indebted to Mr Harold D. Nathan, an undergraduate research assistant, who collected and visually estimated the intensity data. The data were corrected for Lorentz and polarization factors, but no absorption corrections were made. Of the 895 independent reflections within the copper sphere, 730 were collected; of these 23 were too weak to be observed. In addition, three reflections were too strong to be estimated reliably and one (731) was very near the edge of the film; these four data were given zero weight.

The data collected around the two different axes were cross correlated and placed on an absolute scale by Wilson's (1942) statistical method. A Howells, Phillips & Rogers (1950) plot of the data is shown in Fig. 1. This plot indicates the crystal to be noncentrosymmetric; and, therefore, the space group should be *Cc*.

The normalized structure factors $|E|$ (Karle & Karle, 1966*b*) were then calculated by the relationship

$$|E_h|^2 = |F_h|^2 / \varepsilon \sum_{j=1}^N f_{jh}^2 \quad (1)$$

Table 2. Distribution of normalized structure factors

	Observed	Theoretical	
		Centric	Acentric
$\langle E \rangle$	= 0.878	0.798	0.886
$\langle E ^2 - 1 \rangle$	= 0.739	0.968	0.736
$\langle E ^2 - 1 \rangle$	= -0.013	0.000	0.000

<i>K</i>	Probability that $ E $ is larger than <i>K</i>	
	Observed	Theory
1.04	0.31	0.30
1.15	0.26	0.25
1.28	0.19	0.20
1.44	0.11	0.15
1.64	0.08	0.10
1.70	0.07	0.09
1.75	0.06	0.08
1.81	0.04	0.07
1.88	0.03	0.06
1.96	0.02	0.05
2.05	0.01	0.04
2.17	0.01	0.03
2.33	0.007	0.02
2.58	0.003	0.01
2.81	0.001	0.005
3.09	0.001	0.002
3.29	0.001	0.001

where $|F_h|$ is the measured scattering amplitude from which the effects of thermal motion have been removed by the use of an overall temperature parameter of 1.65 Å². The value of ε is unity except for the *h0l* reflections where $\varepsilon = 2$, *N* is the number of atoms in the unit cell, and f_{jh} is the atomic scattering factor for the *j*th atom. The observed and theoretical values for certain statistical averages and distributions of the normalized structure factors are shown in Table 2. A comparison of the observed values with those calculated for centrosymmetric and noncentrosymmetric structures confirms that the space group is the noncentrosymmetric *Cc*.

Phase determination

A general description of the phase determination procedure has been given by Karle & Karle (1966*b*). The mode of attack used in this problem follows closely that used in the determination of the structures of L-arginine dihydrate (Karle & Karle, 1964) and panamine (Karle & Karle, 1966*a*). The starting formula for the phase determination is

$$\varphi_h \approx \langle \varphi_k + \varphi_{h-k} \rangle_{k_r} \quad (2)$$

In principle the average should be taken over all *k*'s, but in practice it was restricted at first to *k*'s corresponding to *E* values greater than 1.5, and finally to those with *E* values greater than 1.35. Initially the phases of three reflections are assigned in order to specify the origin in space group *Cc* (Hauptman & Karle, 1956). The reflections 400, $\bar{2}61$ and $\bar{1}, 15, 1$ were chosen to define the origin because these three reflections have the largest numbers of relationships with the other reflections with large *E* values. Symbols were assigned to the phases of three additional reflections. Finally, a phase of zero was assumed for the reflection 0,18,0 for the following reason. In space group *Cc* reflections 0*k*0 have phase angles of either 0 or π . Formula (2) applied to 0,18,0 has on the right hand side nine terms with *E*'s greater than 1.5, among which seven are of the form $\varphi(h, 9, l) + \varphi(\bar{h}, 9, \bar{l})$. Since $\varphi(h, 9, l) = -\varphi(\bar{h}, 9, \bar{l})$, the phase of 0,18,0 is most probably zero. The initial phase assignments are summa-

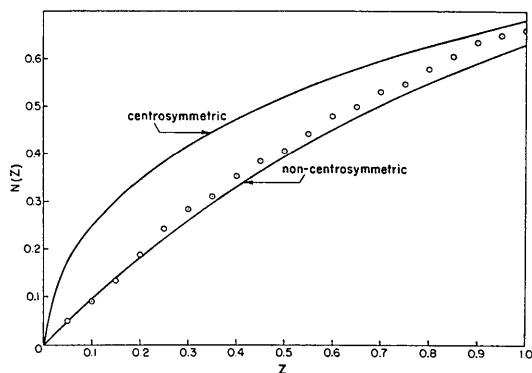


Fig. 1. A Howells, Phillips & Rogers (1950) plot of the data for nitrilotriacetic acid.

rized in Table 3, in which a , b and c may lie anywhere between $-\pi$ and $+\pi$.

Table 3. Initial phase assignments for specifying the origin and utilizing formula (2)

h	k	l	φ	E
4	0	0	$\pi/2$	1.81
2	6	1	$\pi/4$	2.03
1	15	1	$-\pi/4$	1.55
3	15	1	a	1.66
7	15	5	b	2.78
3	17	3	c	1.89
0	18	0	0	1.90

The first stage of phase determination was restricted to the 74 E values larger than 1.5. As new phases were calculated from combinations of the seven assigned reflections they were added to the list of known phases and included in the procedure. This technique was continued, by hand, and resulted in a set of 67 self-consistent phases.

Through the application of formula (2) it was also possible to assign values to a , b and c . As additional terms were included in the right hand side of formula (2) relationships between a , b and c were formed. For example, two terms in the average for the reflection 1,9,0 are $(\pi/4) - a$ and $-\pi/2$, from which it appears that a should have a value near $3\pi/4$. Two terms for the reflection 732 are $-\pi/2$ and $-2c + 2b + (\pi/2)$ and two

terms for 065 are $2c + (\pi/4)$ and $b - \pi$; these relationships indicate that b should have a value near $-\pi/4$ and c near $\pi/4$. Other relationships of this kind confirmed these assignments.

In the next stage the initial set of phases was refined and additional phases were determined by the iterative application of the tangent formula (Karle & Hauptman, 1956),

$$\tan \varphi_h \approx \frac{\sum_k |E_k E_{h-k}| \sin(\varphi_k + \varphi_{h-k})}{\sum_k |E_k E_{h-k}| \cos(\varphi_k + \varphi_{h-k})} \quad (3)$$

A Fortran program was written to calculate $\tan \varphi_h$ values by using the set of known phases in the right hand side of formula (3). The results of each cycle of these calculations were used to form a new list of known phases with which the procedure was repeated. Three such cycles of refinement were required to reach convergence for all phases with E 's greater than 1.5.

These phases were then used to extend the determination to reflections with E values greater than 1.4. After three cycles that included all E 's larger than 1.4 the tangent formula had again converged. In three more cycles phases for all reflections with E values greater than 1.35 had been assigned and refined. After each cycle of these computations a listing of the new phase angles was compared with that obtained in the previous cycle, with the intention of removing any reflections with erratic variations; however, none were observed.

The 114 reflections whose phases had been determined in the method described above were used to calculate the E map that is shown in Fig. 2, the normalized structure factors, E_h , being used as Fourier coefficients. The molecule was easily fitted to this map. A comparison with the phases computed from the final refined structure gave an average error of 46° for 110 reflections, the four $0k0$ reflections being excluded from the average. Fig. 3 shows the distribution of the errors.

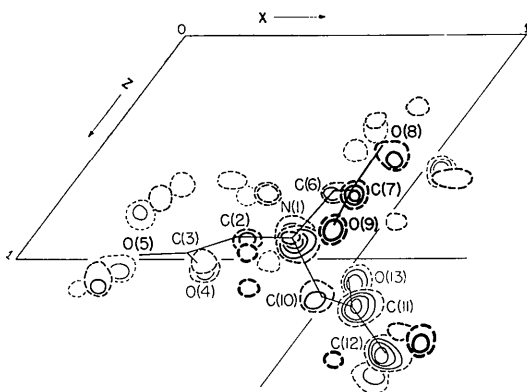


Fig. 2. A composite of sections of a three-dimensional E map viewed down the b axis. The contours are at equal intervals on an arbitrary scale.

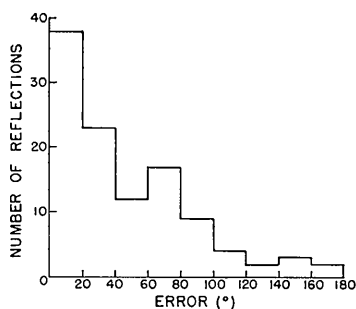


Fig. 3. The distribution of the differences between the phase angles determined by the tangent formula and those calculated for the refined structure.

Refinement of the structure

All calculations below were carried out on an IBM 7094 computer with subprograms operating under the CRYRM system (Duchamp, 1964). The atomic scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1962). The atomic scattering factor for H is that given by Stewart, Davidson & Simpson (1965). The least-squares routine minimizes the quantity $\sum w(F_o^2 - F_c^2)^2$. The weights, w , used throughout the refinement of the structure, were set proportional to $1/\sigma^2(F_o^2)$ which had been calculated during the initial data processing.

Approximate coordinates were obtained from the E map (Fig. 2) for all thirteen of the heavier atoms. In space group Cc the x and z coordinates of the origin are indeterminate. Accordingly, the x and z coordinates for N(1) were held constant throughout the refinement of the structure. The proposed structure was then

hydrogen atoms. The hydrogen atoms bonded to the methylene carbons, C(2), C(6) and C(10), were easily located, but the acidic hydrogen atoms were not evident and they were left for a later stage. The introduction of the six methylene-hydrogen atoms reduced the R index to 9.3%. The positions of these six hydrogen atoms were refined with fixed isotropic temperature parameters of 3.0 \AA^2 .

From the bond distances and angles involving the heavy atoms (Fig. 6) it was apparent that one of the carboxyl groups had equivalent oxygen atoms and dimensions appropriate for the ionized form, while the other two had non-equivalent oxygen atoms and the dimensions expected for the undissociated form. It was therefore surmised that one of the three acidic hydrogen atoms must be bonded to oxygen O(8), the second to oxygen O(12) and the third to the nitrogen atom. The hydrogen atom bonded to the nitrogen was assumed to lie on a line perpendicular to the plane of the centers of atoms C(2), C(6) and C(10) at a distance of 0.9 \AA from the nitrogen. The two remaining hydrogen atoms were located along the lines of apparent hydrogen bonding at a distance of 0.9 \AA from the oxygen atoms to which they are covalently bonded. The introduction of these three additional hydrogen atoms

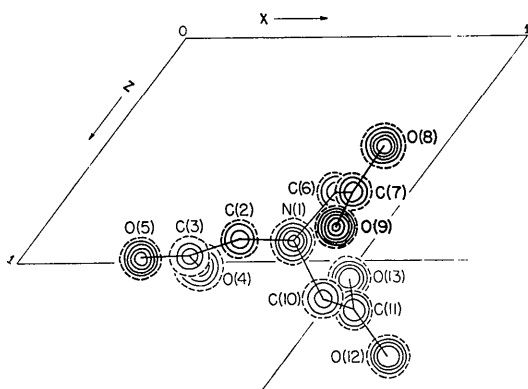


Fig. 4. A composite of sections of a three-dimensional electron density map through each of the heavy-atoms, viewed down the b axis. The dashed contour is at $4 \text{ e.}\text{\AA}^{-3}$. The successive contours are at 6, 8, 10, ... $\text{e.}\text{\AA}^{-3}$.

into the calculations without refinement of their positional or isotropic temperature parameters did not reduce the R index below 9.3%, but the sum of the weighted residuals, $\sum w(F_o^2 - F_c^2)^2$, was decreased by 3%. The observed and calculated structure factors, $|F_o|$ and $|F_c|$, and the phase angles, φ , are listed in Table 4.

The final parameters for the heavy atoms and their standard deviations, calculated from the least-squares residuals, are given in Table 5. The shifts calculated for the parameters in the final cycle of least-squares were all less than one-tenth of the standard deviations. The positional parameters for the hydrogen atoms are given in Table 6.

Table 6. *Coordinates and standard deviations of the hydrogen atoms*

A fixed isotropic temperature factor of 3.0 \AA^2 was assigned to all hydrogen atoms. Those coordinates marked with an asterisk were not refined. The values have been multiplied by 10^3 .

	x	y	z
H(14)	892 (16)	108 (5)	677 (21)
H(15)	656 (16)	101 (5)	503 (21)
H(16)	509 (17)	171 (5)	706 (23)
H(17)	650 (17)	204 (6)	1012 (20)
H(18)	1082 (17)	157 (6)	1217 (22)
H(19)	936 (18)	114 (5)	1324 (23)
H(20)	722*	69*	883*
H(21)	1384*	20*	1458*
H(22)	833*	277*	491*

Description and discussion of the structure

A composite of the final electron density map viewed along the b axis is shown in Fig. 4. An analogous composite of a difference synthesis for which the contributions of the hydrogen atoms were omitted from F_c is shown in Fig. 5. No other peaks in the difference map were as high as those representing hydrogen atoms.

The bond distances and angles involving the heavy atoms are shown in Fig. 6. The standard deviations in the atomic coordinates (Table 5) correspond to positional uncertainties of approximately 0.014 \AA for the heavy atoms. The standard deviations in their bond

Table 5. *Heavy-atom parameters and their standard deviations*

The values have been multiplied by 10^4 . The temperature factor is in the form $T = \exp \{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	7640	1153 (3)	9080	113 (16)	8 (2)	90 (25)	-5 (7)	94 (31)	-16 (9)
C(2)	6001 (17)	1570 (4)	9017 (22)	168 (22)	13 (2)	203 (37)	6 (10)	261 (50)	-6 (12)
C(3)	4913 (17)	1093 (4)	9751 (19)	160 (21)	12 (2)	96 (29)	-6 (9)	118 (42)	-27 (11)
O(4)	5452 (14)	443 (3)	10221 (17)	141 (16)	11 (2)	226 (26)	-3 (7)	158 (33)	15 (10)
O(5)	3540 (17)	1370 (3)	9858 (21)	231 (19)	14 (2)	445 (36)	-22 (9)	494 (47)	-55 (12)
C(6)	7780 (17)	1327 (4)	6942 (20)	135 (21)	9 (2)	193 (33)	-4 (9)	204 (45)	15 (12)
C(7)	8270 (16)	2123 (4)	6932 (21)	91 (17)	13 (2)	189 (33)	18 (10)	134 (41)	31 (13)
O(8)	8220 (13)	2284 (3)	4948 (17)	161 (17)	14 (2)	258 (28)	-19 (8)	291 (36)	2 (10)
O(9)	8574 (14)	2543 (3)	8551 (18)	186 (17)	8 (1)	295 (28)	-18 (8)	329 (37)	-19 (9)
C(10)	9721 (14)	1175 (4)	11709 (20)	80 (18)	10 (2)	201 (35)	-3 (8)	69 (40)	-8 (11)
C(11)	10971 (17)	497 (4)	12186 (20)	137 (21)	10 (2)	126 (31)	-3 (9)	133 (43)	10 (11)
O(12)	12951 (13)	562 (3)	14233 (17)	84 (13)	10 (1)	227 (26)	16 (6)	66 (30)	6 (9)
O(13)	10141 (15)	-17 (3)	10803 (19)	176 (16)	9 (1)	235 (28)	5 (7)	178 (36)	-21 (9)

distances are expected to be about 0.02 Å and the standard deviations in the bond angles about 3° to 4°.

Distances and angles involving the hydrogen atoms are listed in Table 7. The standard deviations of the bond distances involving hydrogen atoms are approximately 0.2 Å.

Table 7. Bond distances and angles involving hydrogen atoms

H(14)-C(6)	1.08 Å	H(16)-C(2)-H(17)	109°
H(15)-C(6)	1.16	H(16)-C(2)-N(1)	96
H(16)-C(2)	1.04	H(16)-C(2)-C(3)	115
H(17)-C(2)	1.07	H(17)-C(2)-N(1)	117
		H(17)-C(2)-C(3)	109
H(18)-C(10)	1.04	H(18)-C(10)-H(19)	114
H(19)-C(10)	1.19	H(18)-C(10)-N(1)	120
		H(18)-C(10)-C(11)	101
H(20)-N(1)	0.90*	H(19)-C(10)-N(1)	107
H(21)-O(12)	0.90*	H(19)-C(10)-C(11)	104
H(22)-O(8)	0.90*		
		H(20)-N(1)-C(2)	105*
		H(20)-N(1)-C(6)	105*
		H(20)-N(1)-C(10)	105*
H(14)-C(6)-H(15)	84°	H(21)-O(12)-C(11)	118
H(14)-C(6)-N(1)	123	H(22)-O(8)-C(7)	108
H(14)-C(6)-C(7)	100		
H(15)-C(6)-N(1)	113		
H(15)-C(6)-C(7)	122		

* Assigned value.

The carboxyl groups are planar within experimental error. The equations of the least-squares planes through the carboxyl groups and the deviations of the individual atoms from their respective planes are given in Table 8. Fig. 7 shows the electron density in the least-squares plane of each of the carboxyl groups.

Table 8. Least-squares planes of the carboxyl groups and atomic deviations from the plane

Coefficients are direction cosines relative to the crystallographic axes.

Plane through atoms C(2), C(3), O(4) and O(5)
 $0.1451X + 0.2217Y + 0.6737Z = 5.2852$

Atom	Deviation
C(2)	0.0002 Å
C(3)	-0.0009
O(4)	0.0003
O(5)	0.0003

Plane through atoms C(6), C(7), O(8) and O(9)
 $0.8079X - 0.2023Y - 0.0567Z = 4.2754$

Atom	Deviation
C(6)	-0.0039
C(7)	0.0146
O(8)	-0.0048
O(9)	-0.0057

Plane through atoms C(10), C(11), O(12) and O(13)
 $-0.7317X - 0.3534Y + 0.9087Z = 0.4522$

Atom	Deviation
C(10)	0.0013
C(11)	-0.0050
O(12)	0.0016
O(13)	0.0020

The bond distances in nitriilotriacetic acid indicate that the group C(3),O(4),O(5) exists as a carboxylate ion. The observed C-O distances can be compared with the average value of 1.25 Å for the formates of sodium, calcium, strontium and barium (Pauling, 1960). The average distances observed for the C-O and C=O bonds of the two remaining carboxyl groups, 1.30 and 1.20 Å, are typical of those for a carboxylic acid (Hahn, 1960). The other distances and angles are all close to the expected values and equivalent bonds are found to have the same lengths within experimental error.

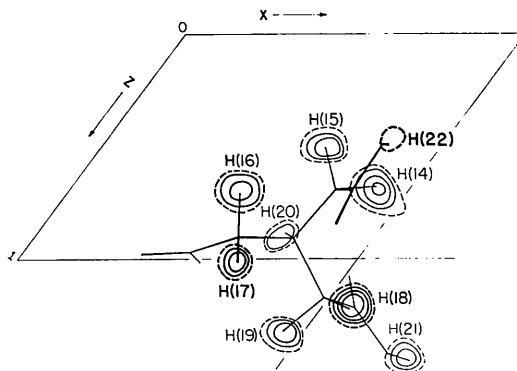


Fig. 5. A composite of sections of a three-dimensional difference Fourier map through each of the hydrogen atoms, viewed down the *b* axis. The dashed contour is at 0.4 e.Å⁻³. The successive contours are at 0.5, 0.6, 0.7, ... e.Å⁻³.

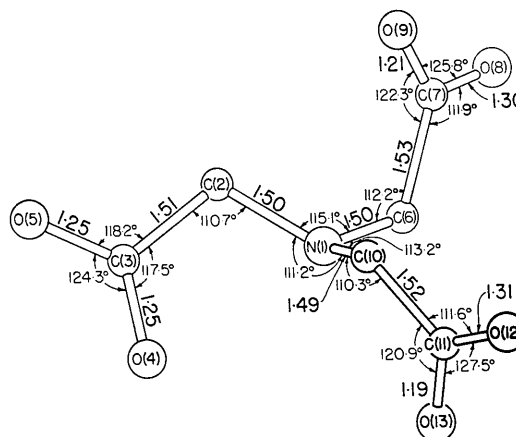


Fig. 6. Bond distances and angles for the heavy atoms of nitriilotriacetic acid.

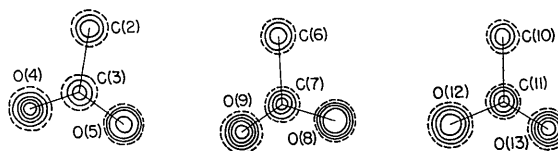


Fig. 7. Electron density plots in the planes of each of the carboxyl groups. The contours are at intervals of 2 e.Å⁻³, beginning with the dashed contour at 4 e.Å⁻³.

A stereoscopic projection of the molecule is shown in Fig. 8. These figures were drawn on a CALCOMP plotter controlled by an IBM 7094 computer with the ORTEP program (Johnson, 1965). From this figure it is clear that H(20) bonded to the nitrogen atom is in close contact with O(4) and O(13), the H...O distances being 2.14 and 2.26 Å, respectively; H(20) is thus in a position to form an almost symmetrical bifurcated hydrogen bond. The distances from these two oxygen atoms to the N(1) atoms are 2.63 and 2.68 Å. This close

approach of the oxygen atoms to the hydrogen may partially explain the rather low third dissociation constant.

Hydrogen atoms H(21) and H(22) are involved in the intermolecular bonding. The distances O(4)···O(12') and O(8)···O(5''), where O(12') and O(5'') are atoms of neighboring molecules, are both observed to be 2.51 Å. This is a short hydrogen-bond distance approaching the value for a symmetrical hydrogen bond. For example, the symmetrical hydrogen bond in po-

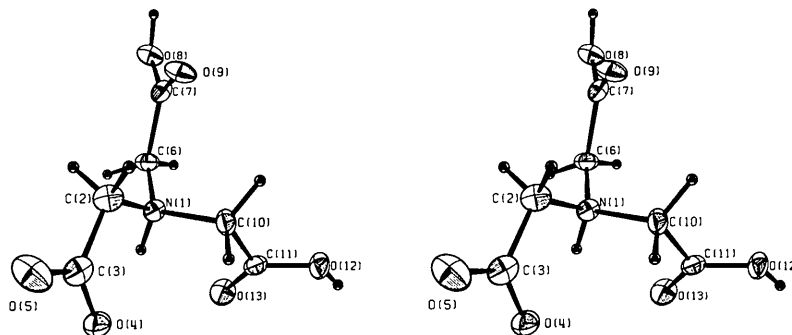


Fig. 8. Stereoscopic view of nitrilotriacetic acid.

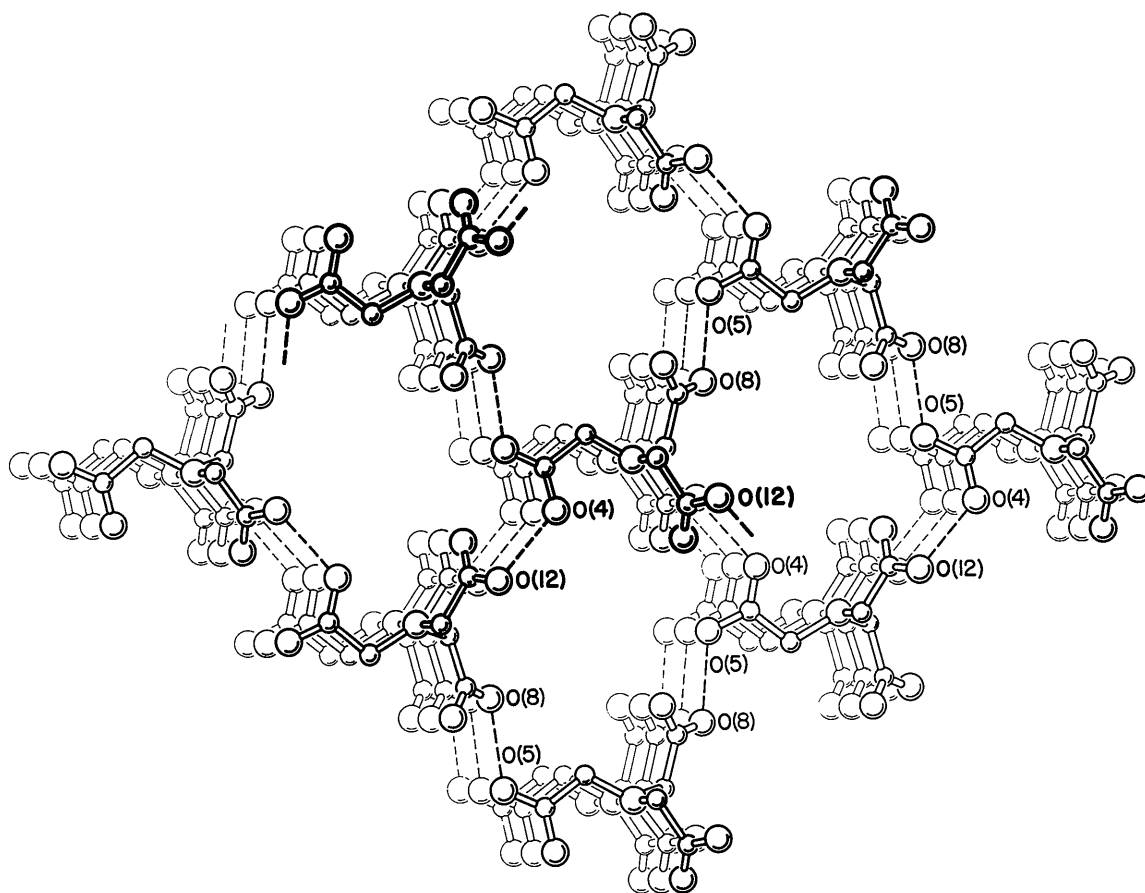


Fig. 9. The hydrogen-bonding network of nitrilotriacetic acid viewed from 3° to the left of the vertical to the *xy* plane. Only half of the molecules are shown. (See text.)

tassium hydrogen chloromaleate is 2.41 Å long (Ellison & Levy, 1965) and in acetamide hemihydrochloride, 2.40 Å (Takei & Hughes, 1955). Hydrogen bonds similar to those in nitrilotriacetic acid are found in cytosine-5-acetic acid, where the hydrogen-bonded O...O distance is observed to be 2.506 Å (Marsh, Bierstedt & Eichhorn, 1962). The high density of nitrilotriacetic acid (1.66 g.cm⁻³) is probably a manifestation of the strong hydrogen bonding.

Fig. 9 shows half of the molecules in the structure which form a hydrogen-bonded network of interconnected right- and left-handed helices with axes approximately normal to the *xy* plane. The molecules which are not shown form a similar network that is interleaved with the one in Fig. 9, the molecules in it being parallel to and equidistant from the molecules shown. The vectors $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, and $\mathbf{c}' = \mathbf{a} + 2\mathbf{c}$ form a nearly orthogonal cell with twice the volume of the chosen cell and with a unique angle β' of 89.7°. In terms of this nearly orthogonal cell the molecules shown on top of each other in Fig. 9 are related by multiples of the translation vector \mathbf{c}' , while those not shown are generated by odd multiples of $\frac{1}{2}\mathbf{c}'$. There is no hydrogen bonding between the two networks.

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A New Structure Type with Octahedron Pairs for Rh₂S₃, Rh₂Se₃ and Ir₂S₃

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The structure of Rh₂S₃ has been determined, using single-crystal data. The space group is *Pbcn* (*D*_{2h}¹⁴) and the lattice constants are $a = 8.462$, $b = 5.985$, $c = 6.138$ Å. The expected octahedral coordination of the rhodium atoms is confirmed. Every octahedron shares a common face with one other octahedron to form octahedron pairs. These octahedron pairs may be imagined to be arranged in layers which show the stacking sequence *ABABA*... Four rhodium atoms surround each sulfur atom at the vertices of a distorted tetrahedron. Isotypic compounds are Ir₂S₃ and Rh₂Se₃. From intensity calculations for Rh₂(S_{1-x}Se_x)₃ it is inferred that a complete range of solid solubility exists between Rh₂S₃ and Rh₂Se₃.

Introduction

Disagreement exists in the literature concerning the structure and composition of the phases in the system Rh-S. In particular, earlier experiments by one of us

showed that all attempts to prepare the reported Rh₂S₃ led to a two-phase mixture containing elementary S and a homogeneous rhodium sulfide phase which was identified to be Rh₂S₃ (Hulliger, 1964). This compound was found to be a diamagnetic semiconductor which