

- HUGHES, R. E. & LAUER, J. L. (1959). *J. Chem. Phys.* **30**, 1165–1170.
- HYNDMAN, D. & ORIGLIO, G. F. (1960). *J. Appl. Phys.* **31**, 1849–1852.
- IWASAKI, M. (1963). *J. Polymer Sci. A1*, 1099–1104.
- LIQUORI, A. M. (1961). *Chimica Inorganica, IV Corso Estivo di Chimica, Varenna*, 1959, pp. 311–333. Ed. Accad. Nazl. Lincei, Roma.
- MCCALL, D. W., DOUGLASS, D. C. & FALCONE, D. R. (1967). *J. Phys. Chem.* **71**, 998–1004.
- MASON, E. A. & RICE, W. E. (1954). *J. Chem. Phys.* **22**, 843–851.
- MAZEE, W. M. (1948). *Rec. Trav. Chim. Pays-Bas*, **67**, 197–213.
- PETRACCONE, V., ALLEGRA, G. & CORRADINI, P. (1972). *J. Polymer Sci. C38*, 419–427.
- RENEKER, D. H. (1962). *J. Polymer Sci.* **59**, S39–42.
- SCOTT, R. A. & SCHERAGA, H. A. (1966a). *J. Chem. Phys.* **44**, 3054–3069.
- SCOTT, R. A. & SCHERAGA, H. A. (1966b). *J. Chem. Phys.* **45**, 2092–2101.

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## The Crystal and Molecular Structure of a Monoclinic Phase of Iminodiacetic Acid

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The crystal and molecular structure of a monoclinic phase of iminodiacetic acid,  $C_4H_7NO_4$ , has been determined from X-ray intensity data obtained with a four-circle diffractometer. The space group is  $P2_1/c$  with  $Z=4$ ,  $a=6.3406$  (7),  $b=9.1364$  (6),  $c=9.3783$  (13) Å and  $\beta=92.72$  (1)°. The structure ( $R=0.040$ ) is a three-dimensional network of 10- and 14-membered rings composed of hydrogen-bonded halves of the iminodiacetic acid molecule. There are three independent hydrogen bonds in the structure. Two of them are of the type  $N-H\cdots O$  with lengths 2.674 (2) and 2.807 (2) Å, and one is of the type  $O-H\cdots O$  with the length 2.536 (2) Å.

### Introduction

The structures of a number of compounds containing the iminodiacetic acid group have been reported. In these structures the iminodiacetic acid residue acts as a monodentate or a tridentate ligand coordinated to lanthanoid(III) ions (Albertsson & Oskarsson, 1968; Oskarsson, 1971) or as a donor of hydrogen bonds to halide ions (Oskarsson, 1973). The organic molecule shows a large conformational variation in these compounds. In order to study the effect of different crystallographic surroundings upon the geometry of the iminodiacetic acid group we have determined the structure of the acid. A comparison with oxydiacetic acid (Herbertsson & Boman, 1973) and thiodiacetic acid (Paul, 1967) should also give some information concerning the effect of the atom (O, S or N) between the acetic acid residues upon packing and hydrogen bonding.

Three different modifications of iminodiacetic acid, denoted  $\alpha$ ,  $\beta$  and  $\gamma$ , have been reported by Tomita, Ando & Ueno (1964). Novak, Cotrait & Jousot-Dubien (1965) have studied the infrared spectrum of iminodiacetic acid in the solid state ( $\alpha$ -phase) and they conclude that it is a zwitterion. In this communication the crystal and molecular structure of a monoclinic phase corresponding to the  $\beta$ -phase is reported and is referred to below as IMDAMO.

### Crystal data

Iminodiacetic acid,  $C_4H_7NO_4$  (IMDAMO); F. W. 133.1; Monoclinic, space group  $P2_1/c$ ;  $a=6.3406$  (7),  $b=9.1364$  (6),  $c=9.3783$  (13) Å,  $\beta=92.72$  (1)°,  $V=542.7$  Å<sup>3</sup>;  $Z=4$ ;  $\mu(Cu K\alpha)=13.0$  cm<sup>-1</sup>;  $D_m=1.64$ ,  $D_x=1.629$  g cm<sup>-3</sup>. Numbers within parentheses represent estimated standard deviations.

### Experimental

Commercial iminodiacetic acid (BDH, Chemicals Ltd., Poole, England) was recrystallized from water by slow evaporation at room temperature. Two colourless solid phases were obtained, one needle-shaped and the other short prismatic. For both phases elemental analyses gave values in good agreement with those calculated for  $C_4H_7NO_4$ . The density  $D_m$  was determined from the loss of weight in benzene. Weissenberg photographs showed the needle-shaped crystals to be orthorhombic and the short prismatic ones to be monoclinic. The systematically absent reflexions for IMDAMO are  $0k0$  with  $k \neq 2n$  and  $h0l$  with  $l \neq 2n$ , which are consistent with the space group  $P2_1/c$ . The unit-cell dimensions were improved by a least-squares treatment of powder spectra obtained with a Guinier-Hägg focusing camera (Cu  $K\alpha_1$  radiation,  $\lambda=1.54051$  Å, 22°C). Alu-

minimum (cubic,  $a=4.04934 \text{ \AA}$ ) was used as internal standard.

A single crystal with dimensions  $0.10 \times 0.18 \times 0.25 \text{ mm}$  was used for data collection on an automatic four-circle diffractometer of type CAD-4 (manufactured by Enraf-Nonius, Delft, Holland). Intensity data were measured at a take-off angle of  $5^\circ$  with Cu  $K\alpha$  radiation. A graphite monochromator was used. The  $\omega$ - $2\theta$  scan technique was employed (moving crystal and moving counter), with a scan interval  $\Delta\omega=0.80+0.50 \tan \theta$ . A fast pre-scan was used to determine the scan speed at which a predetermined minimum number of counts (3000) were received by the detector. The background intensity was measured for  $\frac{1}{4}$  of the scan time at both ends of the interval. All 1031 independent reflexions in the range  $5^\circ < \theta < 70^\circ$  were measured with repeated scans. Of these reflexions, 68 with  $I < 3\sigma_c(I)$  were considered insignificantly different from the background and excluded from the refinement. The values of  $\sigma_c(I)$  were based on counting statistics. The reflexions 200,  $2\bar{1}2$  and  $3\bar{2}4$  were selected as standards, and the intensity of one of them was recorded every hour. The fluctuation in the intensities of the standard reflexions was random and less than 5%. The values of  $I$  and  $\sigma_c(I)$  were corrected for Lorentz, polarization and absorption effects. The expression  $p=(1+\cos^2 2\theta_M \cos^2 2\theta)/(1+\cos^2 2\theta_M)$  with  $\theta_M=13.3^\circ$  was

used in the correction of the polarization effects. The transmission factors evaluated by numerical integration varied from 0.818 to 0.905.

### Structure determination and refinement

The positions of the non-hydrogen atoms were determined by symbolic addition (Karle & Karle, 1963, 1966).

Full matrix least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$  was performed with weights  $w=1/(\sigma_c^2 + a|F_o|^2 + b)$ , where  $a$  and  $b$  were chosen to make the average value of  $w(|F_o| - |F_c|)^2$  almost equal in the different  $|F_o|$  and  $\sin \theta$  intervals. In the last cycles of refinement the values  $a=0.0004$  and  $b=3.0$  were used. The convergence was checked by the agreement indices  $R$  and  $R_w$  defined by  $R=\sum ||F_o| - |F_c||/\sum |F_o|$  and  $R_w=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ . The refinement of the scale factor, the positional parameters, and the anisotropic thermal parameters converged to  $R=0.087$  and  $R_w=0.117$ . All hydrogen atoms except one, H(1), were located in a difference map obtained from data with  $\sin \theta/\lambda \leq 0.5 \text{ \AA}^{-1}$ . At this stage an isotropic extinction parameter (Zachariasen, 1967) and the parameters of the hydrogen atoms found were included in the refinement. The temperature factors obtained for the hydrogen atoms were considered too small and were therefore given the value  $3.0 \text{ \AA}^2$ . The remaining independent hydrogen atom could now be located in a difference map calculated with the  $|F_o|$  values corrected for extinction. This hydrogen atom was included in the refinement with  $B=3.0 \text{ \AA}^2$ . In the last cycle the shifts in the parameters were less than 10% of the estimated standard deviations. The refined value of the extinction parameter  $g=1.75(9) \cdot 10^4$  corresponds to a mosaic spread of  $3.3''$  if the crystal is of type I and a domain size of  $2.70 \cdot 10^{-4} \text{ cm}$  if it is of type II. The final agreement indices obtained were  $R=0.040$  and  $R_w=0.048$ . A final difference map was featureless.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968) for the non-hydrogen atoms and from Hanson, Herman, Lea & Skillman (1964) for the hydrogen atom. The positional and thermal parameters, and the r.m.s. components along the principal axes of the thermal

Table 1. Atomic coordinates with standard deviations ( $\times 10^4$ )

	x	y	z
N	6805 (2)	799 (2)	3087 (2)
O(1)	11894 (2)	685 (2)	1535 (1)
O(2)	8946 (2)	1887 (2)	858 (1)
O(3)	3436 (2)	3756 (1)	4149 (1)
O(4)	3829 (2)	1463 (1)	4909 (1)
C(1)	9141 (3)	650 (2)	3107 (2)
C(2)	9969 (3)	1146 (2)	1694 (2)
C(3)	5995 (3)	2331 (2)	3084 (2)
C(4)	4269 (3)	2496 (2)	4137 (2)
H(1)	12302 (36)	979 (27)	673 (27)
H(2)	6291 (36)	306 (27)	2284 (26)
H(3)	6384 (35)	347 (26)	3921 (25)
H(4)	9803 (35)	1266 (27)	3880 (24)
H(5)	9495 (36)	-355 (29)	3277 (25)
H(6)	7145 (38)	3013 (27)	3431 (25)
H(7)	5458 (36)	2585 (27)	2111 (26)

Table 2. Anisotropic thermal parameters with standard deviations ( $\times 10^4$ )

The form of the temperature factor is  $\exp(-\beta_{11}h^2 - \dots - 2\beta_{12}hk - \dots)$ . The r.m.s. components  $R_i (\times 10^3)$  in  $\text{\AA}$  of thermal displacement along the ellipsoid axes are also listed.

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$R_1$	$R_2$	$R_3$
N	130 (4)	48 (2)	46 (2)	-4 (2)	34 (2)	0 (1)	115 (3)	142 (3)	181 (2)
O(1)	145 (3)	92 (2)	64 (2)	20 (2)	50 (2)	12 (1)	121 (3)	181 (2)	219 (2)
O(2)	164 (4)	118 (2)	64 (2)	23 (2)	38 (2)	34 (1)	133 (3)	178 (2)	247 (2)
O(3)	199 (4)	65 (2)	73 (2)	38 (2)	72 (2)	17 (1)	123 (3)	150 (2)	247 (2)
O(4)	200 (4)	64 (2)	68 (2)	14 (2)	61 (2)	18 (1)	125 (3)	163 (2)	233 (2)
C(1)	133 (4)	69 (2)	55 (2)	17 (2)	26 (2)	9 (1)	138 (3)	155 (3)	193 (3)
C(2)	138 (4)	54 (2)	54 (2)	-9 (2)	26 (2)	-5 (2)	137 (3)	148 (3)	184 (3)
C(3)	135 (4)	52 (2)	56 (2)	6 (2)	28 (2)	3 (2)	136 (3)	147 (3)	183 (3)
C(4)	124 (4)	62 (2)	45 (2)	3 (2)	19 (2)	1 (2)	132 (3)	160 (3)	168 (3)

motion ellipsoids, are given in Tables 1 and 2. Observed and calculated structure factors are given in Table 3. Selected interatomic distances and angles are shown in Table 4.

Table 3. Observed and calculated structure factors

The columns are  $k$ ,  $10|F_o|$  and  $10|F_c|$ .

$k$	$10 F_o $	$10 F_c $
1	100	100
2	100	100
3	100	100
4	100	100
5	100	100
6	100	100
7	100	100
8	100	100
9	100	100
10	100	100
11	100	100
12	100	100
13	100	100
14	100	100
15	100	100
16	100	100
17	100	100
18	100	100
19	100	100
20	100	100
21	100	100
22	100	100
23	100	100
24	100	100
25	100	100
26	100	100
27	100	100
28	100	100
29	100	100
30	100	100
31	100	100
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33	100	100
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35	100	100
36	100	100
37	100	100
38	100	100
39	100	100
40	100	100
41	100	100
42	100	100
43	100	100
44	100	100
45	100	100
46	100	100
47	100	100
48	100	100
49	100	100
50	100	100
51	100	100
52	100	100
53	100	100
54	100	100
55	100	100
56	100	100
57	100	100
58	100	100
59	100	100
60	100	100
61	100	100
62	100	100
63	100	100
64	100	100
65	100	100
66	100	100
67	100	100
68	100	100
69	100	100
70	100	100
71	100	100
72	100	100
73	100	100
74	100	100
75	100	100
76	100	100
77	100	100
78	100	100
79	100	100
80	100	100
81	100	100
82	100	100
83	100	100
84	100	100
85	100	100
86	100	100
87	100	100
88	100	100
89	100	100
90	100	100
91	100	100
92	100	100
93	100	100
94	100	100
95	100	100
96	100	100
97	100	100
98	100	100
99	100	100
100	100	100

Table 4. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in IMDAMO

(a) The iminodiacetic acid molecule			
N—C(1)	1.487 (2)	C(1)—N—C(3)	115.4 (1)
N—C(3)	1.491 (2)	N—C(1)—C(2)	110.4 (1)
C(1)—C(2)	1.517 (2)	N—C(3)—C(4)	110.5 (1)
C(3)—C(4)	1.517 (2)	C(1)—C(2)—O(1)	111.6 (2)
C(2)—O(1)	1.306 (2)	C(1)—C(2)—O(2)	122.6 (2)
C(2)—O(2)	1.202 (2)	O(1)—C(2)—O(2)	125.8 (2)
C(4)—O(3)	1.267 (2)	C(3)—C(4)—O(3)	114.2 (2)
C(4)—O(4)	1.229 (2)	C(3)—C(4)—O(4)	119.9 (2)
N—H(2)	0.93 (3)	O(3)—C(4)—O(4)	125.9 (2)
N—H(3)	0.93 (2)	H(2)—N—H(3)	111 (2)
C(1)—H(4)	1.00 (2)	H(4)—C(1)—H(5)	110 (2)
C(1)—H(5)	0.96 (3)	H(6)—C(3)—H(7)	112 (2)
C(3)—H(6)	1.00 (2)	C(2)—O(1)—H(1)	108 (2)
C(3)—H(7)	0.99 (2)		
O(1)—H(1)	0.89 (3)		
(b) Dihedral angles			
N—C(1)—C(2)—O(2)	17.3 (2)		
N—C(1)—C(2)—O(1)	10.5 (1)		
N—C(3)—C(4)—O(3)	2.9 (1)		
N—C(3)—C(4)—O(4)	4.7 (2)		
(c) The hydrogen bonds			
O(1)···O(3)	2.536 (2)	O(1)—H(1)···O(3)	168 (2)
O(1)···H(1)	0.89 (3)	C(2)—O(1)—H(1)	108 (2)
O(3)···H(1)	1.66 (3)	C(4)—O(3)···H(1)	110 (1)
		H(1)···O(3)···H(2)	123 (1)
N·····O(3)	2.807 (2)	N—H(2)···O(3)	151 (2)
N—H(2)	0.93 (3)	C(1)—N—H(2)	106 (2)
O(3)···H(2)	1.96 (3)	C(3)—N—H(2)	111 (2)
		C(4)—O(3)···H(2)	127 (1)
N·····O(4)	2.674 (2)	N—H(3)···O(4)	149 (2)
N—H(3)	0.93 (2)	C(1)—N—H(3)	106 (1)
O(4)···H(3)	1.99 (2)	C(3)—N—H(3)	108 (1)
		C(4)—O(4)···H(3)	170 (1)

All computations were made on the UNIVAC 1108 computer in Lund, Sweden, and a list of the programs used is given by Oskarsson (1973).

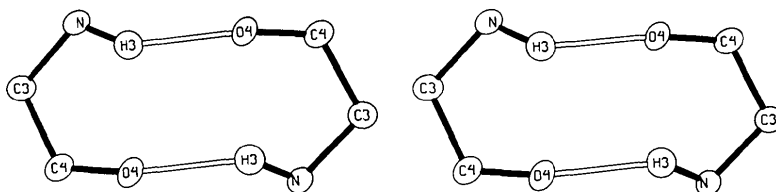


Fig. 1. A stereoscopic view of the 10-membered ring. Figs. 1–5 were drawn by the program ORTEP.

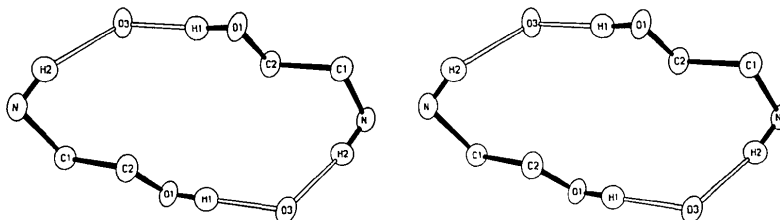


Fig. 2. A stereoscopic view of the 14-membered ring.

### Description of the structure

The most striking feature of the structure is the existence of 10- and 14-membered rings, composed of hydrogen-bonded halves of the iminodiacetic acid molecule. The 10-membered ring (Fig. 1) consists of two molecular halves  $H(3)-N-C(3)-C(4)-O(4)$  related to each other by a centre of symmetry and having an almost planar though slightly chair configuration. The 14-membered ring (Fig. 2) is formed by the other half of the molecule,  $H(2)-N-C(1)-C(2)-O(1)-H(1)$ , the centrosymmetrically related half, and two oxygen atoms  $O(3)$ . In this way a three-dimensional network of 10- and 14-membered rings connected at N and  $O(3)$  is formed, as seen in Fig. 3.

The iminodiacetic acid molecule shown in Fig. 4 is a zwitterion as proposed by Novak *et al.* (1965). The negative charge is most probably spread over the carboxylate group  $O(3)-C(4)-O(4)$ . The dimensions of the other carboxyl group indicate one double bond  $C(2)-O(2)$  and one single bond  $C(2)-O(1)$ . The angle  $C-N-C$  ( $115.4^\circ$ ) is significantly different from the tetrahedral angle, as is also found in iminodiacetic acid hydrochloride and hydrobromide (Oskarsson, 1973). The non-hydrogen atoms of the molecular half, N, C(1), C(2), O(1) and O(2), are almost coplanar (Table 5). The conformation of the molecule around the bonds  $C(1)-C(2)$  and  $C(3)-C(4)$  is shown in Fig. 5(a) and (b). The dihedral angles  $N-C-C-O$  are given in Table 4(b). A detailed discussion of the conformation of the imi-

nodiacetic acid molecule in different crystallographic surroundings is postponed to a later publication.

Table 5. Deviations ( $\text{\AA}$ ) from the least-squares planes through the independent halves in iminodiacetic acid

Atoms defining plane: I N, C(1), C(2), O(1), O(2); II N, C(3), C(4), O(3), O(4). The angle between the planes is  $41^\circ$ .

Atom	I	Atom	II
N	-0.112	N	-0.024
C(1)	0.165	C(3)	0.036
C(2)	0.027	C(4)	-0.004
O(1)	-0.081	O(3)	-0.015
O(2)	0.035	O(4)	0.011

Table 6. Deviations ( $\text{\AA}$ ) from the least-squares planes through the rings

(a) 10-Membered ring	(b) 14-Membered ring		
H(3)	0.097	H(2)	-0.375
N	-0.060	N	-0.365
C(3)	0.071	C(1)	0.322
C(4)	-0.012	C(2)	-0.331
O(4)	-0.080	O(1)	0.438
H(3)	-0.066	H(1)	0.024
N	0.091	O(3)	-0.413
C(3)	-0.041	H(2)	0.375
C(4)	-0.100	N	0.365
O(4)	0.111	C(1)	-0.322
		C(2)	0.331
		O(1)	-0.438
		O(3)	0.413
		H(1)	-0.024

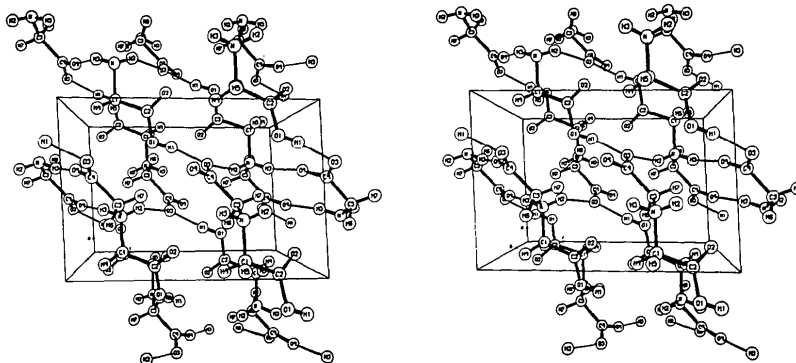


Fig. 3. The structure of IMDAMO with the hydrogen bonds marked by thin lines.

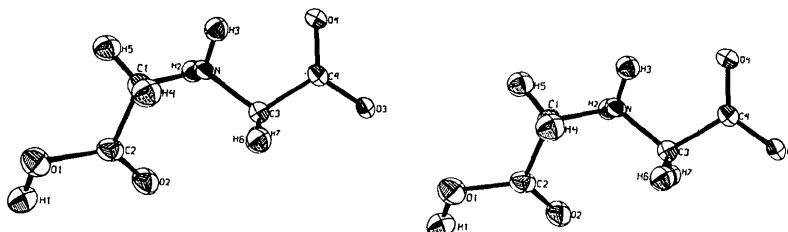


Fig. 4. The iminodiacetic acid molecule in IMDAMO.

The hydrogen-bond system is shown in Fig. 3. The distances and angles involved are summarized in Table 4(c). The three hydrogen atoms in the asymmetric unit which can participate in hydrogen bonding do so. The  $\text{NH}_2$  group donates two hydrogen atoms and the OH group one. The difference between the  $\text{C}(4)\text{--O}(3)$  and  $\text{C}(4)\text{--O}(4)$  distances, 0.038 (3) Å, indicates a more pronounced single-bond character in  $\text{C}(4)\text{--O}(3)$  and this is probably due to the fact that  $\text{O}(3)$  accepts two hydrogen bonds and  $\text{O}(4)$  only one. The bond  $\text{O}(1)\text{--H}(1)\cdots\text{O}(3)$  is asymmetric, with hydrogen-oxygen distances of 0.89 (3) and 1.66 (3) Å and with an oxygen-oxygen distance of 2.536 (2) Å.

In the structures of oxydiacetic acid,  $\text{C}_4\text{H}_6\text{O}_5$ , and thioldiacetic acid,  $\text{C}_4\text{H}_6\text{O}_4\text{S}$ , the molecules form infinite chains by hydrogen bonding in pairs of carboxyl groups around a centre of symmetry (Herbertsson & Boman, 1973; Paul, 1967). In this way 8-membered rings are formed. In iminodiacetic acid the situation is more complex, since the carboxyl groups are non-equivalent and the nitrogen atom takes part in hydrogen bonding.

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#### References

- ALBERTSSON, J. & OSKARSSON, Å. (1968). *Acta Chem. Scand.* **22**, 1700–1702.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- HERBERTSSON, H. & BOMAN, C. E. (1973). To be published. *International Tables for X-ray Crystallography*. (1968). Vol. III. 2nd ed., pp. 202–206. Birmingham: Kynoch Press.
- KARLE, J. & KARLE, I. L. (1963). *Acta Cryst.* **16**, 969–975.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.
- NOVAK, A., COTRAIT, M. & JOUSSOT-DUBIEN, J. (1965). *Bull. Chim. France*, pp. 1808–1812.
- PAUL, S. (1967). *Acta Cryst.* **23**, 491–494.
- OSKARSSON, Å. (1971). *Acta Chem. Scand.* **25**, 1206–1216.
- OSKARSSON, Å. (1973). *Acta Cryst.* **B29**, 1747–1751.
- TOMITA, Y., ANDO, T. & UENO, K. (1965). *Bull. Chem. Soc. Japan*, **38**, 138–139.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

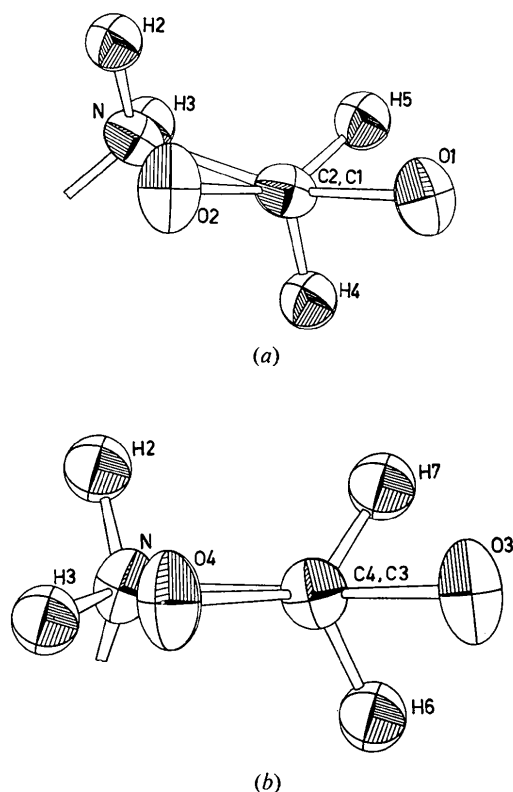


Fig. 5. The two molecule halves viewed along the C-C bonds. The values of the dihedral angles are given in Table 4(b).