

shown by comparison of the relevant torsion angles given in Table 4.

The molecules form centrosymmetric dimers similar to those found in spiperone: $N(1)-H \cdots O(27)$: 2.865 \AA [$O(27)$: $-x, 1-y, 2-z$].

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SHORT COMMUNICATIONS

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Crystallographic and spectroscopic studies on ethylenediaminetetraacetic acid (EDTA). II. Comparison of two structure determinations of β -EDTA. By M. F. C. LADD and D. C. POVEY, *Department of Chemical Physics, University of Surrey, Guildford, Surrey, England*

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Two structure determinations of β -EDTA are compared and the hydrogen atom positions and bonding discussed.

Recently, we published a structure determination of β -ethylenediaminetetraacetic acid (β -EDTA) (Ladd & Povey, 1973). Subsequently, our attention was drawn to another report on the structure of the same compound (Cotrait, 1972) which pre-dates our paper.

It is interesting to compare the two structure determinations. Fig. 1 is a schematic drawing of one half of the EDTA molecule, to relate the two atom-numbering schemes. In each investigation similar amounts of reflexion data were collected from small crystals on a Siemens four-circle diffractometer, using $Cu K\alpha$ radiation, and corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods and refined by least-squares calculations with the programs of Ahmed (Cotrait) and the X-RAY 70 system (Ladd & Povey). A selection of general structural data is listed in Table 1. Three of the reflexions, $\bar{1}52$, 517 and $\bar{1}4,2,6$, used in each starting set were the same, although their magnitudes differed by about 15%.

In each structure, the hydrogen atoms were located on a difference map. Cotrait refined the coordinates of the hydrogen atoms with a fixed isotropic temperature factor of 2 \AA^2 for each. Ladd & Povey did not refine these coordinates and allocated isotropic temperature factors 0.5 \AA^2 higher ($1.8-3.0 \text{ \AA}^2$) than those of the carbon atoms to which they are bonded.

Because of certain differences in the two sets of bond lengths we re-calculated Cotrait's values using his published data and the *BONDLA* program of the X-RAY 70 system.

Table 1. *Structural data for β -EDTA*

	Cotrait (1972)	Ladd & Povey (1973)
a (\AA)	13.286 (2)	13.273 (4)
b	5.578 (5)	5.575 (7)
c	16.120 (3)	16.110 (6)
β ($^\circ$)	96.30 (5)	96.26 (3)
V_c (\AA^3)	1188	1185 (2)
D_m (g cm^{-3})	1.65 (2)	1.65 (1)
D_c	1.635	1.638 (3)
Z	4	4
Space group	$C2/c$	$C2/c$
Crystal dimensions (mm)	0.2, 0.3, 0.3	0.1, 0.4, 0.1
Number of reflexions	1203	1020
Final R	5.3%	5.6%

The results are presented in Table 2,* with his original values and our own with estimated standard deviations corrected from those reported in our 1973 paper.

The differences in the bond lengths among the heavier atoms, columns (b) and (c) in Table 2, are not significant ($< 3\sigma$). Bonds involving hydrogen show greater discrepancies. The two Cotrait sets are slightly different, especially where hydrogen atoms are involved. Our C-H and N-H bond lengths are all appreciably longer. We agree with Cotrait, and contrary to our previous paper, that there are three hydrogen bonds of similar importance involving the nitrogen atom.

* Cotrait's atom numbering has been used throughout.

Table 2. Bond lengths and hydrogen bonds (Å) in β -EDTA

A prime indicates an atom related to that in Fig. 1 by the twofold axis through the central C-C bond

	(a)	(b)	(c)
C(2)-C(2')	1.512 (2)	1.512 (2)	1.508 (5)
N(1)-C(2)	1.505 (2)	1.505 (2)	1.511 (5)
N(1)-C(3)	1.508 (2)	1.508 (2)	1.512 (5)
N(1)-C(7)	1.497 (2)	1.497 (2)	1.494 (5)
C(3)-C(4)	1.518 (2)	1.517 (2)	1.502 (5)
C(7)-C(8)	1.526 (2)	1.526 (2)	1.516 (5)
C(4)-O(5)	1.273 (2)	1.273 (2)	1.272 (5)
C(4)-O(6)	1.235 (2)	1.235 (2)	1.235 (5)
C(8)-O(9)	1.288 (2)	1.287 (2)	1.288 (5)
C(8)-O(10)	1.212 (2)	1.211 (2)	1.214 (5)
N(1)-H(17)	0.911 (28)	0.911 (29)	0.972
C(2)-H(11)	0.941 (34)	0.922 (34)	0.999
C(2)-H(12)	0.965 (29)	0.920 (30)	1.003
C(7)-H(13)	0.957 (29)	0.968 (29)	1.002
C(7)-H(14)	0.974 (28)	0.785 (28)	1.057
C(3)-H(15)	0.939 (29)	0.953 (31)	1.023
C(3)-H(16)	0.969 (30)	0.917 (27)	1.009
C(8)-H(14)	-	0.784 (29)	-
O(6)-H(17)	2.329 (28)	2.329 (29)	2.271
O(6')-H(17)	2.149 (28)	1.950 (29)	1.908
O(10)-H(17)	2.387 (29)	2.387 (28)	2.379
O(5')-H(18)	1.284 (30)	1.285 (28)	1.286
O(9')-H(18)	1.197 (27)	1.197 (28)	1.197
N(1)-O(6)	2.748 (2)	-	2.751 (4)
N(1)-O(6')	2.787 (2)	-	2.780 (5)
N(1)-O(10)	2.682 (2)	-	2.675 (4)
O(9)-O(5')	2.460 (2)	-	2.458 (5)

(a) Cotrait (1972).

(b) Cotrait (1972), recalculated.

(c) Ladd & Povey (1973). Correction of an error in $\sigma(\cos \theta)$ has led to small changes in the e.s.d.'s of the bond lengths and bond angles; the revised values are reported here.

The source of the scattering factor data for hydrogen, used by Cotrait, is not listed. Stewart, Davidson & Simpson (1965) have discussed the refinement of hydrogen-atom parameters. A study of the literature shows that even with their scattering factors, refined C-H bond lengths frequently vary widely and are appreciably different from the standard values (Sutton, 1965).

The average value for terminal C-H bonds, obtained from difference maps is about 0.99 Å, 0.08–0.1 Å less than the standard values. Refinement tends to reduce their value further, because of the high asymmetry of the electron density around hydrogen.

In β -EDTA, hydrogen atoms are of two types: the terminal atoms such as H(11) and H(13), to which situation Stewart *et al.* (1965) addressed themselves, and the hydrogen-bonded hydrogen atoms such as H(18) and H(18'), to which isolated-atom scattering factors are more applicable.

The refinement of terminal hydrogen-atom parameters by the method of least squares may be justified inasmuch as it produces the best fit of the model to the data, but in such circumstances the C-H bond lengths may have little credence. We suggest that, where possible, the hydrogen-atom positional coordinates are best determined by calculation from the molecular geometry and standard C-H distances.

The differences in the e.s.d.'s of the bond lengths arise from the fact that the e.s.d.'s on our x , y , and z coordinates are about twice those given by Cotrait. We consider that this situation may be occasioned by both the difference in the number of 'unobserved' reflexions and variations between block-diagonal and full-matrix refinements (Rollett, 1970).

The bond angles are listed in Table 3. There is one notable discrepancy in the C(2')-C(2)-N(1) angle, but there are no

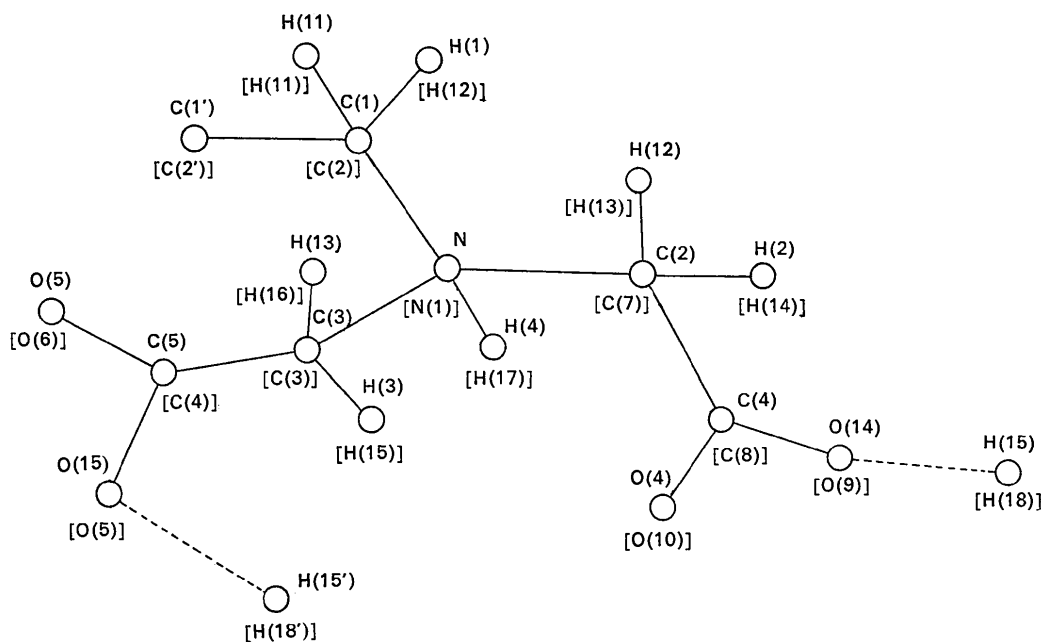


Fig. 1. Schematic diagram of one-half of the EDTA molecule. Cotrait's numbering is given in square brackets.

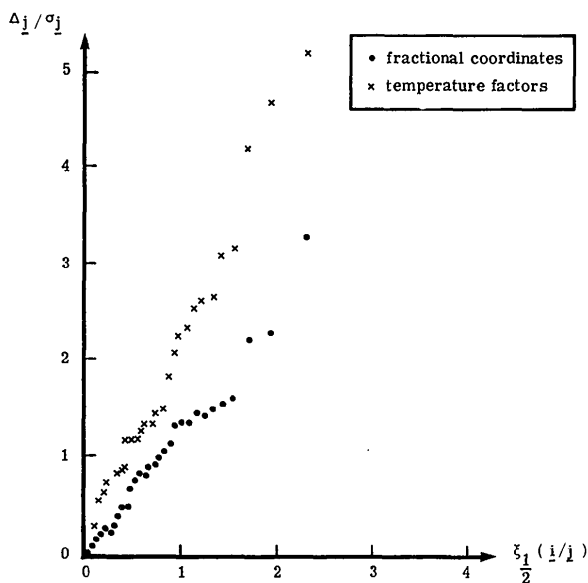


Fig. 2. Half-normal probability plots for fractional positional coordinates and anisotropic temperature factors (β_{kk}).

other comments to make which are not vested in the discussion already given. There were no e.s.d.'s on the bond angles given by Cotrait (1972) but they have emerged in our re-calculation of his results.

In order to make our comparison of the two structure reports more quantitative, we have calculated half-normal probability plots (Abrahams & Keve, 1971; Abrahams, 1972) for the positional coordinates and anisotropic temperature factors (β_{kk}).

For each set of parameters, the ordered, experimental values of Δ_j/σ_j are plotted against their expectation values, $\xi_{1/2}(i/j)$ (Hamilton & Abrahams, 1972). Δ_j is the numerical difference between corresponding j th parameters, and σ_j^2 is the sum of the variances in the two parameters under consideration; $\xi_{1/2}(i/j)$ is the expectation value of the i th largest value of Δ_j/σ in a sample of j observations having zero mean and unit variance.

The results are illustrated in Fig. 2. A completely random normal distribution of errors leads to a linear plot of unit slope and zero intercept. In this application, the plots are approximately linear, pass through the origin and have slopes of about 1.3 and 2.2 for the positional coordinates and temperature factors, respectively. It may be concluded

Table 3. Bond angles ($^\circ$) in β -EDTA

A prime indicates an atom related to that in Fig. 1 by the twofold axis through the central C-C bond.

	(a)*	(b)*	(c)*
C(2')-C(2)-N(1)	110.30	115.78 (13)	115.94 (29)
C(2)-N(1)-C(7)	108.21	108.36 (13)	108.82 (28)
C(7)-N(1)-C(3)	110.20	110.33 (13)	110.54 (30)
C(2)-N(1)-C(3)	115.03	115.07 (13)	114.74 (27)
N(1)-C(3)-C(4)	111.55	111.92 (13)	112.73 (27)
C(3)-C(4)-O(5)	113.50	113.84 (13)	113.95 (29)
C(3)-C(4)-O(6)	120.28	120.47 (14)	120.49 (32)
O(5)-C(4)-O(6)	125.41	125.68 (16)	125.53 (35)
N(1)-C(7)-C(8)	109.58	109.98 (13)	110.13 (31)
C(7)-C(8)-O(10)	119.30	119.50 (15)	119.61 (34)
O(9)-C(8)-O(10)	125.16	125.27 (16)	125.00 (33)
C(7)-C(8)-O(9)	115.10	115.18 (14)	115.35 (31)
C(7)-N(1)-H(17)	109.53	109.88 (177)	112.04
C(3)-N(1)-H(17)	108.43	108.73 (189)	105.27
C(2)-N(1)-H(17)	104.16	104.26 (178)	105.34
H(11)-C(2)-H(12)	106.26	106.43 (295)	107.77
H(15)-C(3)-H(16)	110.13	110.22 (248)	110.51
H(13)-C(7)-H(14)	98.50	98.72 (266)	110.57
C(8)-O(9)-H(18)	112.60	113.00 (126)	113.43

* See footnote to Table 2

that systematic errors in both structure determinations are negligible but that the standard deviations of the positional coordinates and temperature factors have been underestimated by about 1.3 and 2.2, respectively.

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