not been observed on the difference synthesis calculated for this atom.

The molecular packing is illustrated in Fig. 2. The shortest intermolecular contacts between the tetrafluoroborate and the benzothiazolium molecule range between 2·95 and 3·27 Å. Some nonbonded interactions are reflected in the short contacts between either S and F(3), 2·95 (1) Å, or C(2) and F(3′), 2·97 (2) Å, as well as between the methyl C(10) and F(4), 3·19 (2) Å. If we adopt the values of 1·85, 1·35, 1·70 and 2·00 Å for the van der Waals radii of S, F, C and the methyl group, the sum of the van der Waals radii for the S–F contact is 3·20 Å, for C–F is 3·05 Å and for the methyl–F contact is 3·35 Å.

We are grateful to Dr C. Stora for her encouragement throughout the work. We thank Dr H. Larivé, Director of Kodak Pathé Laboratories, for his keen interest and Dr R. Dennilauler for providing the crystals.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

FERRÉ, Y., VINCENT, E. J., LARIVÉ, H. & METZGER, J. (1973). *Bull. Soc. Chim. Fr.* pp. 1003–1013.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HARLOW, R. L., SIMONSEN, S., PFLUGER, C. E. & SAMES, M. P. (1974). *Acta Cryst.* B**30**, 2264–2267.

KARLE, I. L., DRAGONETTE, K. S. & BRENNER, S. A. (1965). *Acta Cryst.* **19**, 713–716.

MILER SRENGER, E. (1974). *Acta Cryst.* B**30**, 1911–1914.

PLETCHER, J., SAX, M., SENGUPTA, S., CHU, J. & YOO, C. S. (1972). *Acta Cryst.* B**28**, 2928–2935.

POWER, L., PLETCHER, J. & SAX, M. (1970). *Acta Cryst.* B**26**, 143–148.

STEWART, R. F., DAVIDSON, E.R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1978). B**34**, 588–593

The Structure of Chaetoglobosin A: A Novel Use of Quartet Invariants

BY J. V. SILVERTON* AND C. KABUTO †

Laboratory of Chemistry, National Heart, Lung, and Blood Institute, National Institutes of Health, Bethesda, MD 20014, *USA*

AND T. AKIYAMA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

(*Received* 17 *May* 1977; *accepted* 26 *September* 1977)

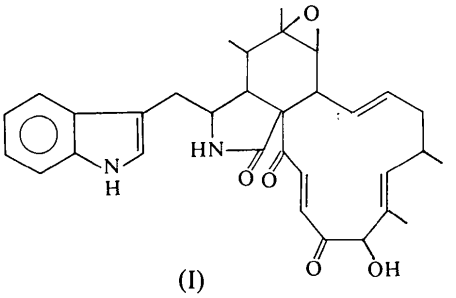
The mycotoxin, chaetoglobosin A, crystallizes in space group $P2_12_12_1$ with four formula units, $C_{32}H_{36}N_2O_5.H_2O$, in a unit cell with dimensions $a = 10{\cdot}036$ (1), $b = 16{\cdot}888$ (1) and $c = 17{\cdot}092$ (2) Å. The structure was determined by direct methods, making use of a technique which uses the reflections occurring most often in the negative quartets as a starting set in the multi-solution approach, and refined to $R = 0{\cdot}033$ using 3207 reflexions measured with an automatic diffractometer. The absolute configuration has also been determined by means of the anomalous scattering of oxygen and proves to be the same as that of the 11-cytochalasins.

Introduction

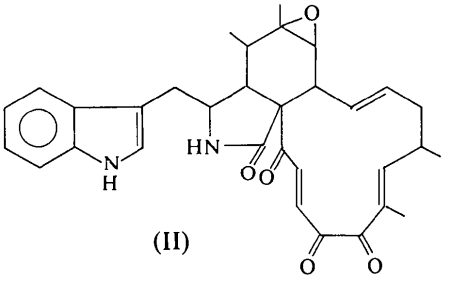
A brief communication by Silverton, Akiyama, Kabuto, Sekita, Yoshihira & Natori (1976) reported the structure of chaetoglobosin A (I) and gave references to previous chemical work on chaetoglobosins (A–F). The basic reasons for attempting the structure determination were to prove the structure and to determine the absolute configuration. The structure of another compound of this class, chaetoglobosin C (CHETC) (II), was determined independently by Springer, Clardy, Well, Cole, Kirksey, MacFarlane and Torgerson (1976).

* To whom correspondence should be addressed.

† Permanent address: Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai, Japan.



(I)



(II)

Data collection and solution of the phase problem

Experimental techniques and data-collection methods were standard for this laboratory and details are given in Table 1. Except as otherwise stated, computer programs used were those of the XRAY 72 system of Stewart, Kruger, Ammon, Dickinson & Hall (1972). Lorentz and polarization corrections were applied to the X-ray data using programs written by Silverton, but no absorption corrections were used.

Many attempts were made to solve the structure using standard symbolic addition and also symbolic addition with limited sets of triples indicated as most probable by the calculation of structure invariants (Hauptman, 1972) but, although the solutions were apparently consistent, it was not possible to recognize significant parts of the molecule. Multisolution approaches using the *MULTAN* system of Main, Woolfson & Germain (1971) were also used, again without success, although they confirmed a previous impression that the difficulties were possibly connected with a lack of strongly interacting origin-defining reflexions. None of the solutions were particularly outstanding on the bases of the tests included in *MULTAN*.

At this point it was decided to try the use of quartet invariants in their application *via* NQEST (De Titta, Edmonds, Langs & Hauptman, 1975). Some 200 potentially negative quartets were evaluated by a program of Silverton & Kabuto (1975) using the $P1$ formula of Hauptman (1975). It was recognized that the $P1$ formula might not be completely reliable in $P2_12_12_1$ but it was the only one available. The criteria used, in the terminology of De Titta, Edmonds, Langs & Hauptman (1975), were $B > 0{\cdot}25$, $E_{\text{cross}} < 0{\cdot}7$. The last of the multisolution attempts gave rise to 32 results, which were tested using local programs (Silverton & Kabuto, 1975) for NQEST. With 200 quartets, there was one solution with a negative value of NQEST (−0·08) but the corresponding E map did not show recognizable molecular fragments. Similar results were obtained with 110 quartets having $B \geq 0{\cdot}28$ and 80 with $B \geq 0{\cdot}3$.

It was then decided to attempt an approach for which the original hope was only that it might allow NQEST to have its maximum effect. Since the correct solution should have the most negative NQEST and those planes occurring most often in the quartets have the greatest effect on NQEST, it seemed reasonable to use the small set of commonly occurring planes as the starting set for a multisolution approach. The experimental results also indicated that such a starting set would be radically different from those previously tried.

The planes (6,0,17), (7,18,0), (0,1,11) and (0,8,11) occurred fairly frequently in the set of 200 potentially negative quartets and were used to select the origin and enantiomorph. The planes (2,12,10) (1,5,14) and (4,12,17) were of frequent occurrence and were used as variable phases. There were thus 64 solutions using *MULTAN*. It was necessary to use three variables since the above planes do not interact very strongly and are

Table 1. *Crystal and experimental data*

Chaetoglobosin A
Formula: $C_{32}H_{36}N_2O_5$
$M_r = 528{\cdot}65$
Asymmetric unit: $C_{32}H_{36}N_2O_5.H_2O$
Asymmetric unit weight: 546·66
Space group: $P2_12_12_1$
Cell dimensions: from LS refinement of $\pm\theta$ data
Radiation: Cu $K\alpha$, graphite monochromator, $\lambda = 1{\cdot}5418$ Å
$a = 10{\cdot}036$ (1) Å
$b = 16{\cdot}888$ (1)
$c = 17{\cdot}092$ (2)
$D_m = 1{\cdot}25$ (1) g cm^{-3}
$D_x = 1{\cdot}25$
Crystal size: ellipsoid 0·35 × 0·3 × 0·3 mm
Reflections: 3207 (468 unobserved: 1σ)
Maximum sin θ/λ: 0·6163 Å^{-1}
Diffractometer: Enraf–Nonius CAD-4
LS weighting: after Peterson & Levy (1957)
Scattering factors: C, N, O, Cromer & Mann (1968); H, Stewart, Davidson & Simpson (1965)
R(observed reflections only): 0·033
Dispersion corrections

	Real	Imaginary
N	0·029	0·018
C	0·017	0·009
O	0·047	0·032

by no means obvious starting values for symbolic addition or multisolution. For this structure determination, we selected two-dimensional planes (not necessarily the commonest planes in the quartets) to define the origin and enantiomorph. Later work appears to indicate that this restriction was unnecessary.

Among the 64 solutions, in gratifying contrast to the previous results, there was one obviously best answer using the *MULTAN* criteria: ABSFOM: 1·0962 (highest), PSIZERO: $0{\cdot}2001 \times 10^3$ (lowest) and R_k: 36·24% (lowest). This solution was also indicated by NQEST. Using only quartets with $B > 0{\cdot}3$, NQEST was −0·21 and the other solutions gave values of −0·10 to +0·50, and with $B > 0{\cdot}29$ NQEST was −0·17; other solutions ranged from −0·08 to +0·44. The situation became less definite with smaller values of B. It will be noted that the discrimination given by NQEST was considerably better than in the previous attempts, attesting to the value of the test for selecting a correct solution if one exists.

The indicated solution gave rise to 41 chemically reasonable peaks, 39 of which were correct and the whole molecule, apart from substituent groups, was visible in the E map. Some initial confusion was caused by the presence of an additional atom, O(s), which, from the criteria of physical reasonableness, significance tests and the presence of appropriate peaks attributable to H, was later deduced to be the O atom of an unexpected water molecule.

Structure refinement and determination of absolute configuration

Sequential least-squares refinement and difference maps allowed rejection of the incorrect atoms and recognition of those missing. All H atoms were found and the structure was refined by a blocked least-squares approach, with isotropic thermal parameters for the H atoms and anisotropic parameters for the others, to an R factor of 0·033.

While it was expected that the absolute stereochemistry of chaetoglobosin A would be similar to that of the 11-cytochalasins to which it is chemically related and whose absolute configuration is known (Tsukuda & Koyama, 1972; Buchi, Kitaura, Yuan, Wright, Clardy, Demain, Glinsukin, Hunt & Wogan, 1973), there is no direct evidence and, therefore, both possible enantiomers were refined using anomalous-scattering factors for C, N and O. The expected enantiomer gave the lower R factor but the difference was not significant. The method of Engel (1972) was then applied by selecting 17 planes with $F_o > 20{\cdot}0$, structure factor ratios for the enantiomers, $(F+/F-)$, greater than 1·003 or less than 0·997, and $0{\cdot}96 < (F_o/F_c) < 1{\cdot}04$. The adjacent planes, used to calculate local absorption factors, had similar agreement factors, $F_o > 30{\cdot}0$, $0{\cdot}9995 < (F+/F-) < 1{\cdot}0005$ and had the same h indices as the measured plane but k and l indices differing by at most one unit. Sufficient repetitions were used to achieve a total count on each measurement of 50 000. The absolute stereochemistry was that indicated in Fig. 1 and is the same as that of the 11-cytochalasins. The probability indicated by the χ^2 test is 0·999. In this paper, in an attempt to clarify the stereochemistry near C(23), the molecule is rotated by about 180° around a horizontal axis in comparison with the corresponding diagram of Silverton, Akiyama, Kabuto, Sekita, Yoshihira & Natori (1976).

The atomic parameters are given in Tables 2 and 3.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33059 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Coordinates* (×10⁴) *for the heavier atoms*

	x	y	z
C(1)	8032 (2)	6623 (1)	7891 (1)
O(1′)	7533 (2)	6004 (1)	7647 (1)
N(2)	8212 (3)	6811 (1)	8637 (1)
C(3)	8898 (2)	7561 (1)	8789 (1)
C(4)	9365 (2)	7817 (1)	7962 (1)
C(5)	9288 (2)	8709 (1)	7781 (1)
C(6)	7852 (2)	8983 (1)	7888 (1)
O	7150 (2)	9243 (1)	7187 (1)
C(7)	6873 (2)	8465 (1)	7508 (1)
C(8)	7351 (2)	7783 (1)	6988 (1)
C(9)	8537 (1)	7310 (1)	7383 (1)
C(10)	10026 (2)	7440 (1)	9374 (1)
C(11)	10326 (3)	9196 (1)	8214 (2)
C(12)	7482 (3)	9474 (1)	8591 (2)
C(13)	6175 (2)	7293 (1)	6726 (1)
C(14)	5689 (2)	7301 (1)	6012 (1)
C(15)	4484 (2)	6844 (1)	5740 (1)
C(16)	4788 (2)	6322 (1)	5025 (1)
C(16′)	3565 (2)	5838 (2)	4784 (1)
C(17)	5951 (2)	5784 (1)	5203 (1)
C(18)	6965 (2)	5604 (1)	4740 (1)
C(18′)	7141 (3)	5900 (2)	3915 (1)
C(19)	8061 (2)	5067 (1)	5039 (1)
O(19′)	8188 (2)	4366 (1)	4582 (1)
C(20)	9391 (2)	5501 (1)	5033 (1)
O(20′)	10230 (3)	5318 (1)	4552 (1)
C(21)	9683 (2)	6144 (1)	5593 (1)
C(22)	8930 (2)	6381 (1)	6174 (1)
C(23)	9419 (2)	7020 (1)	6709 (1)
O(23′)	10499 (2)	7325 (1)	6590 (1)
N(1′)	9010 (2)	6447 (1)	11215 (1)
C(2′)	9559 (3)	6445 (1)	10470 (1)
C(3′)	9557 (2)	7191 (1)	10169 (1)
C(3′a)	8972 (2)	7692 (1)	10753 (1)
C(4′)	8705 (2)	8503 (1)	10799 (1)
C(5′)	8163 (3)	8811 (2)	11473 (2)
C(6′)	7872 (3)	8321 (2)	12111 (2)
C(7′)	8109 (2)	7517 (2)	12087 (1)
C(7′a)	8662 (2)	7206 (1)	11406 (1)
O(s)	9351 (2)	5147 (1)	12297 (1)

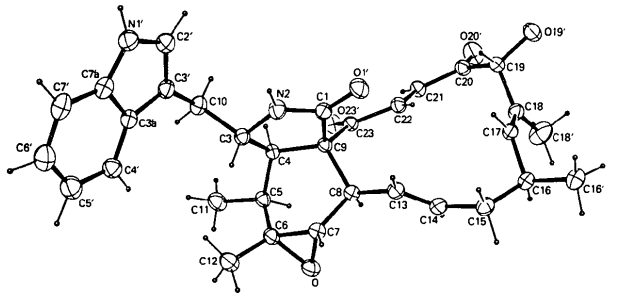


Fig. 1. The molecule of chaetoglobosin A in its crystal conformation. 40% probability ellipsoids are shown for the heavier atoms but those for the H atoms are arbitrary.

Molecular structure and packing

Bond lengths and angles (Fig. 2) do not appear to show any very unusual features and corresponding values are very similar to those deposited as supplemental material with the CHETC structure. In both this structure and CHETC, the aliphatic six-membered ring adopts the boat conformation as may be seen from the torsion angles of the bonds involving C(4) through C(9) (Table 4). The angles are not identical, however, the conformation being somewhat less symmetric in the present structure. The conformations of the two pyrrolidinone rings are also different. The torsion angles indicate that

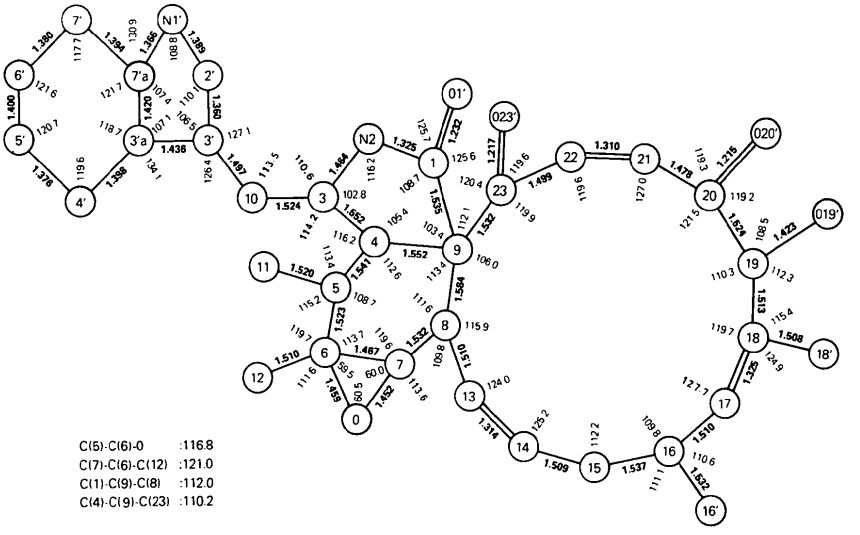


Fig. 2. Bond lengths (Å) and angles (°) for chaetoglobosin A. E.s.d.'s of bond lengths are <0·003 Å except for C(4)–C(5), C(5)–C(6) and C(6)–C(7) where the e.s.d. is less than 0·004 Å. E.s.d.'s of angles are less than 0·25°

Table 3. *Atomic parameters for hydrogen atoms* ($\times 10^3$)

	x	y	z	U(Å^2)		x	y	z	U(Å^2)
H(N2)	788 (2)	646 (1)	902 (1)	48 (6)	H(C16′)*a*	276 (2)	619 (1)	478 (1)	57 (7)
H(C3)	825 (2)	792 (1)	900 (1)	48 (6)	H(C16′)*b*	331 (3)	543 (2)	516 (2)	84 (9)
H(C4)	1037 (2)	761 (1)	789 (1)	55 (6)	H(C16′)*c*	371 (3)	555 (2)	426 (2)	84 (9)
H(C5)	936 (2)	877 (1)	719 (1)	38 (5)	H(C17)	593 (2)	557 (1)	570 (1)	30 (5)
H(C7)	595 (2)	843 (1)	773 (1)	49 (6)	H(C18′)*a*	804 (4)	595 (2)	369 (2)	114 (13)
H(C8)	774 (2)	805 (1)	652 (1)	34 (5)	H(C18′)*b*	647 (3)	626 (2)	375 (2)	109 (11)
H(C10)*a*	1052 (2)	793 (1)	945 (1)	50 (6)	H(C18′)*c*	709 (5)	542 (2)	358 (3)	155 (16)
H(C10)*b*	1063 (2)	707 (1)	915 (1)	44 (6)	H(C19)	784 (2)	490 (1)	558 (1)	35 (5)
H(C11)*a*	1127 (3)	901 (2)	808 (2)	80 (9)	H(O19′)	888 (3)	441 (2)	436 (2)	80 (9)
H(C11)*b*	1032 (4)	974 (2)	805 (2)	107 (11)	H(C21)	1054 (3)	642 (1)	550 (1)	58 (7)
H(C11)*c*	1017 (3)	917 (2)	881 (2)	77 (8)	H(C22)	811 (2)	616 (1)	628 (1)	51 (6)
H(C12)*a*	775 (3)	920 (2)	908 (2)	78 (9)	H(N1′)	901 (3)	600 (2)	1151 (2)	70 (8)
H(C12)*b*	650 (3)	964 (2)	860 (2)	76 (8)	H(C2′)	995 (2)	595 (1)	1021 (1)	59 (7)
H(C12)*c*	799 (2)	1002 (1)	853 (2)	72 (8)	H(C4′)	888 (2)	886 (1)	1033 (1)	48 (6)
H(C13)	572 (2)	698 (1)	711 (1)	47 (6)	H(C5′)	801 (3)	942 (2)	1151 (2)	98 (10)
H(C14)	615 (2)	757 (1)	560 (1)	55 (7)	H(C6′)	751 (3)	854 (1)	1260 (1)	61 (7)
H(C15)*a*	420 (2)	650 (1)	620 (1)	44 (6)	H(C7′)	792 (3)	718 (2)	1253 (2)	84 (9)
H(C15)*b*	375 (3)	722 (2)	559 (2)	89 (9)	H1(Os)	885 (4)	476 (2)	1244 (2)	116 (12)
H(C16)	500 (2)	667 (1)	462 (1)	43 (6)	H2(Os)	1001 (5)	516 (2)	1250 (3)	141 (14)

the rings actually have enantiomeric conformations. The parameters of Altona, Geise & Romers (1968) agree with this deduction. For chaetoglobosins A and C one has φ_m parameters of 20·1 and 18·6° respectively, indicative of the similar bond lengths, but the Δ parameters are −54·3 and +59·7°. In the 13-membered rings, the regions extending from C(22) to C(18) are fairly similar in chaetoglobosins A and C. The conformation of the remainder is necessarily different because of the additional double bond, C(21)–C(22), and the O(19′)–O(20′) hydrogen bond in chaetoglobosin A. Without implying that the crystal conformation represents the lowest energy state for the 13-membered ring, H–H contacts are all satisfactorily large. It will be noted that the three double bonds of this ring are *trans*.

Table 4. *Torsion angles* (°) *for chaetoglobosins A and C*

				A	C					A	C
1	2	3	4	−8	15	14	15	16	17	55	56
2	3	4	9	16	−19	15	16	17	18	−138	−112
3	4	9	1	−18	17	16	17	18	19	178	177
4	9	1	2	14	−10	17	18	19	20	−119	−13
9	1	2	3	−4	−3	18	19	20	21	71	−112
1′	1	9	23	−47	−71	19	20	21	22	5	83
9	4	5	6	64	44	20	21	22	23	177	−83
4	5	6	7	−47	−52	21	22	23	9	179	−168
11	5	6	12	−22	−26	22	23	9	8	−70	−118
5	6	7	8	−6	3	23	9	8	13	86	56
6	7	8	9	45	51	14	15	16	16′	178	178
7	8	9	4	−26	−56	18	17	16	16′	99	126
8	9	4	5	−25	11	18′	18	19	19′	−61	−14
9	8	13	14	−126	−123	19′	19	20	20′	15	−108
8	13	14	15	−177	176	21	22	23	23′	2	30
13	14	15	16	−126	−131	8	9	23	23′	107	61

Table 5. *Possible hydrogen bonds*

X	H	*Y*	*X*···*Y*	∠*XHY*	H···*Y*
N(1′)–H(N1′)···O(*s*)			2·891 Å	167°	1·994 Å
O(*s*)–H1(Os)···O(1′)			2·780	169	1·941
N(2)–H(N2)···O(19′)			2·923	163	2·012
O(19′)–H(O19′)···O(20′)			2·604	126	2·052
O(*s*)–H2(Os)···O			3·118	154	2·414

There are five close approaches of non-bonded atoms which might be due to hydrogen bonds (Table 5). The last can probably be eliminated on the basis of the non-bonded O···H distance. Intermolecular distances, apart from atoms linked by hydrogen bonds, correspond to van der Waals contacts. A sequence of hydrogen bonds, coextensive with the crystal domains, N(2)···O(19′) and N(1′)···O(*s*)···O(1′), links the molecules along the *c* screw axis (Fig. 3).

Further use of the negative-quartet method and conclusions

Since this structure was determined, the method of selecting a starting set has been applied to two other problems, where, although symbolic addition and multi-solution methods gave apparently consistent results, *E* maps were uninformative and NQEST did not indicate significant discrimination. One structure was a comparably sized molecule in space group $A2$ (Kabuto, Silverton, Akiyama, Sankawa, Hutchison, Steyn & Vleggar, 1976) and the other was a compound of molecular weight 810 in space group $P2_12_12_1$ (Silverton & Akiyama, 1977). In both cases, starting sets for the multisolution approach were chosen from reflections prominent in the negative quartets. Solutions were obtained, indicated as most likely by all criteria, which showed most of the atoms in the molecules.

It is intended to continue testing the method in any future problems where standard methods fail and, while the fundamental significance of the technique may be debatable, it may have value, as a referee has pointed out, in selecting a feasible path different from those indicated by standard approaches.

We wish to thank Dr S. Natori, National Institute of Hygienic Sciences, Tokyo, Japan, who suggested the problem, Mr W. Vincent of NIH, DCRT, who implemented the XRAY 72 programs, Mr P. Kalkowski of NIH, DCRT, who implemented *MULTAN*, Dr G. J. B. Williams, Brookhaven National Laboratory, who supplied the *MULTAN* tape, and Mr M. T. Lee, who wrote an acentric symbolic addition program which was used in the earlier work.

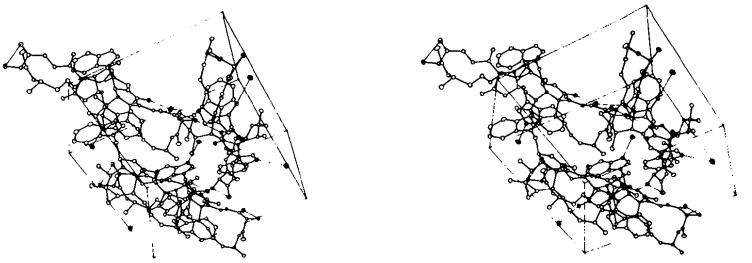


Fig. 3. Packing diagram showing hydrogen bonds.

References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–22.

BUCHI, G., KITAURA, Y., YUAN, S. S., WRIGHT, H. E., CLARDY, J., DEMAIN, A. L., GLINSUKIN, T., HUNT, N. & WOGAN, G. N. (1973). *J. Am. Chem. Soc.* **95**, 5423–5425.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DE TITTA, G. T., EDMONDS, J. E., LANGS, D. A. & HAUPTMAN, H. A. (1975). *Acta Cryst.* A**31**, 472–479.

ENGEL, D. W. (1972). *Acta Cryst.* B**28**, 1496–1509.

HAUPTMAN, H. A. (1972). *Crystal Structure Determination.* New York: Plenum.

HAUPTMAN, H. A. (1975). *Acta Cryst.* A**31**, 680–687.

KABUTO, C., SILVERTON, J. V., AKIYAMA, T., SANKAWA, V., HUTCHISON, R. D., STEYN, P. S. & VLEGGAR, R. (1976). *J. Chem. Soc. Chem. Commun.* pp. 728–279.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN, A Computer Program for the Automatic Solution of Crystal Structures.* Univs. of York, England, and Louvain, Belgium.

PETERSON, S. W. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 70–76.

SILVERTON, J. V. & AKIYAMA, T. (1977). Unpublished results.

SILVERTON, J. V., AKIYAMA, T., KABUTO, C., SEKITA, S., YOSHIHIRA, K. & NATORI, S. (1976). *Tetrahedron Lett.* pp. 1349–1350.

SILVERTON, J. V. & KABUTO, C. (1975). Unpublished programs.

SPRINGER, J. P., CLARDY, J., WELL, J. M., COLE, R. J., KIRKSEY, J. W., MACFARLANE, R. D. & TORGERSON, D. F. (1976). *Tetrahedron Lett.* pp. 1355–1358.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system–version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TSUKUDA, Y. & KOYAMA, H. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 739–744.

Acta Cryst. (1978). B**34**, 593–597

The Crystal and Molecular Structures of Two Derivatives of a Spiro-oxazolone: a *cis vs trans* X-ray Study

BY M. L. MARTÍNEZ, F. H. CANO AND S. GARCÍA-BLANCO

Departamento de Rayos X, Instituto de Química-Física 'Rocasolano', Serrano 119, *Madrid* 6, *Spain*

(*Received* 27 *June* 1977; *accepted* 23 *September* 1977)

The typical *cis–trans* ambiguity for two spiro-oxazolone derivatives has been solved. The compounds ($C_{17}H_{13}O_2N$) crystallize in space groups $P2_1/c$ and $P\bar{1}$, respectively, with $Z = 4$ and 2, in unit cells of dimensions: $a = 5{\cdot}988$ (2), $b = 10{\cdot}703$ (4), $c = 21{\cdot}338$ (8) Å, $\beta = 94{\cdot}12$ (2)° and $a = 11{\cdot}099$ (2), $b = 11{\cdot}182$ (2), $c = 5{\cdot}482$ (1) Å, $\alpha = 82{\cdot}39$ (2), $\beta = 95{\cdot}43$ (2), $\gamma = 94{\cdot}26$ (2)°. Direct methods followed by Fourier and then least-squares analysis, gave final R factors of 0·045 and 0·042, respectively, for the 970 and 2036 observed reflections. Half-normal probability analysis has been used to compare the two compounds.

Introduction

At the Centro Nacional de Química Orgánica (CSIC Madrid) a search is being carried out for a suitable synthetic route of 1-aminocyclopropane carboxylic acids, compounds that are believed to be of interest for interfering with the biochemistry of naturally occurring amino acids. In particular 1-amino-2-arylcyclopropane carboxylic acids could be useful as substrates as well as inhibitors of dopadecarboxylase, a key enzyme in the synthesis of biogenic amines. One of the pathways studied was the known oxazolone synthesis of amino acids. It was found that the *cis* and *trans* isomers of 2-phenyl-4-benzylidineoxazolin-5-one, on

Table 1. *Crystallographic data for cis- and trans-DOAS*

	cis-DOAS	*trans*-DOAS
Formula	$C_{17}H_{13}O_2N$	$C_{17}H_{13}O_2N$
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
μ	0·89 cm^{-1}	0·89 cm^{-1}
Size	0·1 × 0·2 × 0·3 mm	0·6 × 0·2 × 0·3 mm
a	5·988 (2) Å	11·099 (2) Å
b	10·703 (4)	11·182 (2)
c	21·338 (8)	5·4816 (5)
α	–	82·39 (2)°
β	94·12 (1)°	95·43 (2)
γ	–	94·26 (2)
V	1364·0 (8) Å^3	670·0 (5) Å^3