

The Cl atom in the chlorovinylidene group is *anti* [or (*E*)] to the phenyl group on C(5), confirming the result of the stereospecific reaction discussed previously.

The molecules are arranged in the structure by normal van der Waals contacts. No anomaly was found in intermolecular distances.

The diffraction data used in this study were collected at the Brookhaven National Laboratory. One of the authors (WJleN) acknowledges support by the National Science Foundation, NSF-CHE-7512847.

Acta Cryst. (1978). **B34**, 3436–3438

The Structure of the Free Acid of Antibiotic A204A

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(Received 3 March 1978; accepted 11 July 1978)

Abstract. $C_{49}H_{84}O_{17} \cdot H_2O \cdot C_3H_6O$, monoclinic, *C*2, $a = 27.576$ (2), $b = 14.711$ (1), $c = 14.348$ (1) Å, $\beta = 92.573$ (4)°, $Z = 4$ and $\rho_c = 1.167$ g cm⁻³. The compound crystallizes in a 1:1:1 ratio with water and acetone. While the overall conformation of the solvated ionophore resembles that of the Na and Ag ion complexes, changes in the hydrogen-bonding scheme are observed.

Introduction. Single crystals of uncomplexed A204A (Fig. 1) were grown from a water/acetone solution. A total of 4513 independent data ($\sin \theta_{\max}/\lambda = 0.562$ Å⁻¹) were collected on an Enraf–Nonius CAD-4 diffractometer using Ni-filtered Cu radiation from a single crystal of dimensions 0.12 × 0.22 × 0.80 mm. Intensities were corrected for Lorentz and polarization factors but not for extinction or absorption [$\mu(\text{Cu } K\alpha) = 7.32$ cm⁻¹]. On the basis of a $2\sigma(I)$ test, 3735 intensities were considered observed. The variance of each F was calculated according to the method of Stout & Jensen (1968) $\{\sigma^2(F) = k/4(Lp)I[\sigma^2(I) + (0.06I)^2]; w(F) = 1/\sigma^2(F)\}$. Unobserved data were assigned weights of zero.

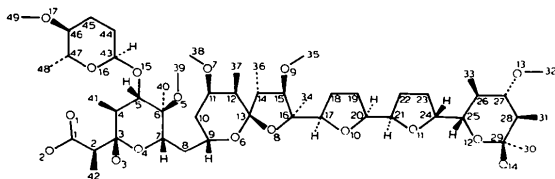


Fig. 1. Chemical structure of A204A and numbering scheme.

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The structure was solved through the use of the direct-methods program *QTAN* (Langs & De Titta, 1975). Although the residual and negative quartet figures of merit would have ultimately allowed the selection of the correct solution, an unambiguous choice of the solution was made possible by eliminating triples identified as unreliable through estimates of the triple invariants based on the ten-magnitude second neighborhood (Kruger, Green & Hauptman, 1977). A total of 48 atoms were correctly identified from the initial *E* map. Subsequent Fourier refinement revealed the positions of the remaining atoms; the acetone molecule was located with considerable difficulty because of its high thermal motion. The structure was

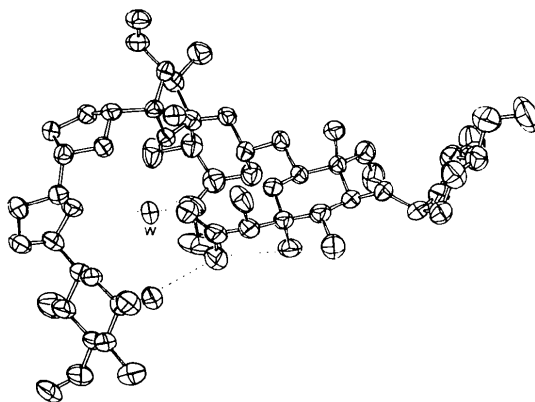


Fig. 2. Observed conformation of A204A with ellipsoids plotted at 50% probability.

Table 1. Positional parameters for nonhydrogen atoms (standard deviations in parentheses)

	x	y	z		x	y	z
C(1)	0.8439 (3)	0.8782 (8)	0.8829 (5)	C(37)	0.8489 (3)	0.5832 (7)	0.5125 (8)
C(2)	0.8546 (3)	0.9775 (7)	0.8984 (5)	C(38)	0.9213 (5)	0.6408 (14)	0.7466 (9)
C(3)	0.8992 (3)	1.0010 (6)	0.8429 (5)	C(39)	1.0168 (3)	1.0487 (9)	0.6269 (7)
C(4)	0.9150 (3)	1.1006 (6)	0.8492 (5)	C(40)	0.8965 (3)	1.1565 (6)	0.6427 (6)
C(5)	0.9538 (2)	1.1206 (6)	0.7795 (5)	C(41)	0.9314 (4)	1.1280 (8)	0.9470 (6)
C(6)	0.9367 (2)	1.0927 (6)	0.6798 (5)	C(42)	0.8104 (3)	1.0388 (7)	0.8756 (7)
C(7)	0.9197 (2)	0.9917 (6)	0.6819 (4)	C(43)	1.0126 (3)	1.2423 (7)	0.8104 (5)
C(8)	0.8965 (3)	0.9577 (6)	0.5901 (5)	C(44)	1.0120 (4)	1.3315 (8)	0.8553 (6)
C(9)	0.8832 (3)	0.8584 (5)	0.5915 (5)	C(45)	0.9950 (4)	1.4018 (7)	0.7849 (7)
C(10)	0.9262 (3)	0.7939 (7)	0.5927 (6)	C(46)	1.0297 (4)	1.3984 (7)	0.7047 (7)
C(11)	0.9076 (3)	0.6965 (7)	0.5887 (7)	C(47)	1.0277 (3)	1.3047 (7)	0.6631 (6)
C(12)	0.8703 (3)	0.6809 (6)	0.5108 (6)	C(48)	1.0625 (4)	1.2954 (10)	0.5850 (8)
C(13)	0.8309 (3)	0.7599 (0)	0.5046 (5)	C(49)	1.0391 (6)	1.5399 (12)	0.6275 (13)
C(14)	0.7971 (3)	0.7522 (6)	0.4173 (5)	O(1)	0.8753 (2)	0.8180 (5)	0.9035 (5)
C(15)	0.7557 (3)	0.8126 (6)	0.4486 (5)	O(2)	0.8012 (2)	0.8585 (5)	0.8470 (5)
C(16)	0.7537 (2)	0.7912 (5)	0.5540 (5)	O(3)	0.9389 (2)	0.9462 (5)	0.8688 (4)
C(17)	0.7108 (2)	0.7279 (6)	0.5752 (5)	O(4)	0.8834 (2)	0.9810 (4)	0.7488 (3)
C(18)	0.7128 (3)	0.6296 (6)	0.5396 (5)	O(5)	0.9734 (2)	1.1042 (4)	0.6151 (3)
C(19)	0.6768 (3)	0.5828 (6)	0.6032 (5)	O(6)	0.8530 (2)	0.8427 (3)	0.5086 (3)
C(20)	0.6792 (3)	0.6382 (6)	0.6925 (5)	O(7)	0.8876 (2)	0.6727 (5)	0.6744 (4)
C(21)	0.6990 (3)	0.5916 (6)	0.7772 (5)	O(8)	0.7986 (2)	0.7446 (3)	0.5792 (3)
C(22)	0.6673 (3)	0.5171 (6)	0.8145 (6)	O(9)	0.7130 (2)	0.7924 (4)	0.3929 (3)
C(23)	0.7028 (3)	0.4588 (6)	0.8686 (6)	O(10)	0.7099 (2)	0.7153 (4)	0.6753 (3)
C(24)	0.7516 (3)	0.4714 (6)	0.8206 (5)	O(11)	0.7433 (2)	0.5475 (4)	0.7577 (4)
C(25)	0.7950 (3)	0.4913 (6)	0.8845 (5)	O(12)	0.7823 (2)	0.5658 (4)	0.9404 (3)
C(26)	0.8101 (3)	0.4082 (7)	0.9455 (6)	O(13)	0.8681 (2)	0.3670 (5)	1.0747 (5)
C(27)	0.8516 (3)	0.4412 (7)	1.0171 (6)	O(14)	0.8614 (2)	0.6234 (5)	0.9554 (4)
C(28)	0.8351 (3)	0.5254 (7)	1.0721 (6)	O(15)	0.9645 (2)	1.2149 (4)	0.7841 (3)
C(29)	0.8211 (3)	0.5986 (6)	1.0036 (6)	O(16)	1.0431 (2)	1.2425 (5)	0.7352 (4)
C(30)	0.7991 (4)	0.6801 (7)	1.0508 (6)	O(17)	1.0102 (3)	1.4615 (6)	0.6343 (6)
C(31)	0.8732 (5)	0.5545 (11)	1.1443 (8)	O(1 <i>W</i>)	0.8076 (2)	0.6988 (4)	0.7770 (4)
C(32)	0.8363 (5)	0.3307 (9)	1.1376 (8)	C(1 <i>S</i>)	0.4566 (8)	0.297 (2)	0.171 (1)
C(33)	0.8270 (5)	0.3274 (8)	0.8866 (9)	C(2 <i>S</i>)	0.4389 (7)	0.379 (2)	0.136 (1)
C(34)	0.7504 (3)	0.8795 (6)	0.6131 (6)	C(3 <i>S</i>)	0.4764 (12)	0.238 (2)	0.109 (2)
C(35)	0.6781 (3)	0.8671 (7)	0.3883 (6)	O(1 <i>S</i>)	0.4538 (7)	0.264 (2)	0.252 (1)
C(36)	0.8203 (4)	0.7851 (7)	0.3257 (6)				

refined by full-matrix least squares treating the vibration of the acetone molecule isotropically and the remainder of the nonhydrogen atoms anisotropically.

Although over half of the H-atom positions could be located from a difference map, their contributions were included for the final three cycles of least-squares refinement by calculating their positional parameters at the end of each cycle; it was not possible to locate the water or hydroxy H atoms. The refinement converged to a residual ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.066 for the observed data and 0.090 for all data; the weighted residual $\{R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}\}$ was calculated to be 0.097 and the standard deviation of an observation of unit weight [$S^2 = \sum w\Delta^2 / (m - n)$ where m is the number of observations and n is the number of parameters] was found to be 2.22.

Positional parameters are given in Table 1.

Discussion. A comparison of the conformation of the uncomplexed ionophore as observed in this study (Fig. 2) with that of the Na or Ag ion complex of A204A (Jones, Chaney, Chamberlin, Hamill & Chen, 1973)

reveals small and subtle changes which are most apparent from a comparison of the intramolecular hydrogen-bonding schemes. While the complexed form has an ion bound in a central cavity by O atoms and a strong 'head to tail' hydrogen bond (2.69 Å), the uncomplexed form contains a hydrogen-bonded water molecule in the cavity and has a very weak 'head to tail' hydrogen bond (2.99 Å). Observed water-oxygen distances are compared with the Na-O distances (Jones, Chaney, Chamberlin, Hamill & Chen, 1973) in Table 2. This alteration of the hydrogen-bonding scheme is the result of small changes in the torsion angles of the backbone of the molecule acting in a concerted fashion. The largest of these changes is 8°, and there are as few as four of nineteen bonds which have undergone rotation of 4° or more. Bond distances and angles are unexceptional.*

* Lists of bond distances, bond angles, torsion angles, structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33702 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances from the oxygen atoms of the ionophore to the water molecule compared with the corresponding distances to the sodium ion for the complexed form (Jones *et al.*, 1973) (Å)

	H ₂ O	Na ⁺		H ₂ O	Na ⁺
O(1)	3.09	2.97	O(10)	3.02	2.85
O(2)	2.56	2.71	O(11)	2.85	2.76
O(7)	2.73	2.72	O(12)	3.16	3.12
O(8)	2.92	2.74	O(14)	3.10	3.17

Two intramolecular hydrogen bonds are observed. The double-bonded O atom of the carboxyl group, O(1), is a hydrogen-bond acceptor from both hydroxy groups O(3), 2.64 Å, and O(14), 2.99 Å. The latter is the familiar 'head to tail' hydrogen bond which serves to stabilize the overall conformation of the complex; the former hydrogen bond is a short-range one and serves to lock the carboxyl end of the molecule into a specific conformation so that the other O atom is optimally located for interaction with either the water molecule or an ion. The water molecule accepts a hydrogen bond from the carboxyl group [O(1W)···O(2), 2.56 Å] and

donates protons to O(7), 2.73 Å, and O(11), 2.85 Å. In addition, there is also a close contact between the water molecule and O(8), 2.92 Å. The acetone molecule is not involved in any contacts of less than 3.4 Å and the closest contact between adjacent A204A molecules is 3.45 Å.

This investigation was supported by Grant No. GM19684 awarded by the National Institute of General Medical Sciences, DHEW. We also thank Dr D. Rohrer for the supervision of data collection and Dr Robert J. Hosley of Lilly Research Laboratories for providing us with the sample of uncomplexed A204A.

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Acta Cryst. (1978). **B34**, 3438–3441

The π -Molecular Complex Stilbene-(*sym*-Trinitrobenzene)₂

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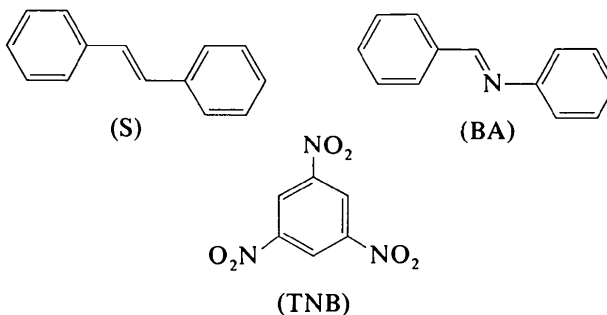
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(Received 23 March 1978; accepted 26 June 1978)

Abstract. C₁₄H₁₂·(C₆H₃N₃O₆)₂, triclinic, $P\bar{1}$, $a = 12.407$ (10), $b = 7.634$ (6), $c = 7.421$ (2) Å, $\alpha = 105.89$ (5), $\beta = 85.68$ (5), $\gamma = 92.03$ (5)°, one complex per cell, $D_m = 1.49$, $D_c = 1.493$ g cm⁻³. Yellow prismatic crystals elongated along c were grown from chloroform at 5°C. Stacks with each phenyl ring of the stilbene sandwiched between two translationally equivalent acceptor molecules extend in the c direction; the ethylene portion of the donor appears to be uncomplexed. The stilbene molecule exhibits signs of disorder similar to that found in all previous stilbene structures.

Introduction. Among the many 'additive compounds' prepared by Sudborough (1910, 1916) were the 1:2 complexes formed between the isoelectronic analogues *trans*-stilbene (S) and benzylideneaniline (BA) with trinitrobenzene (TNB).



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