

Tabelle 6. Winkel innerhalb einer Jodatgruppe

| Atom 1 | Atom 2 | Atom 3 | Winkel(°) | Fehler(°) |
|--------|--------|--------|-----------|-----------|
| O(1) | O(2) | O(3) | 63,0 | 0,3 |
| O(2) | O(1) | O(3) | 59,5 | 0,3 |
| O(1) | O(3) | O(2) | 57,5 | 0,3 |
| O(1) | J | O(2) | 92,8 | 0,4 |
| O(1) | J | O(3) | 102,2 | 0,3 |
| O(2) | J | O(3) | 95,3 | 0,4 |

Die Packungsdichte im $K_2Ge(IO_3)_6$ ist typisch für Jodatstrukturen. Die Raumerfüllung beträgt ca. 51% gegenüber 74% in einer dichtesten Sauerstoffpackung.

Die für die Steuerung und Auswertung der Diffraktometermessungen notwendigen Programme stellte uns dankenswerterweise Herr Professor Dr G. Ruban zur Verfügung. Die übrigen Rechnungen wurden mit Programmen des Systems X-ray 63 (*X-ray Handbook*, 1965) am DRZ in Darmstadt durchgeführt.

Herrn Professor Dr K. Plieth danken wir sehr herzlich dafür, dass er uns Messzeit am Vierkreisdiffraktometer des Instituts für Kristallografie (FU Berlin) ein-

geräumt hat, den Herrn Dr W. Dreissig und Dr P. Luger schulden wir Dank für ihre Unterstützung bei der Durchführung der Messungen und Rechnungen.

Dem Verband der Chemischen Industrie danken wir für die finanzielle Förderung der Untersuchungen.

Literatur

- BILTZ, W. (1934). *Raumchemie der festen Stoffe*. Leipzig: Akademische Verlagsgesellschaft.
- CROMER, D. T. & LARSON, A. C. (1956). *Acta Cryst.* **9**, 1015.
- DASENT, W. E. & WADDINGTON, T. C. (1960). *J. Chem. Soc.* p. 2429.
- FRYDRYCH, R. (1969). Habilitationsschrift, Freie Universität, Berlin.
- IBERS, J. A. (1956). *Acta Cryst.* **9**, 225.
- International Tables for X-ray Crystallography* (1962). Vol. III. pp. 160–165, 202–216. Birmingham: Kynoch Press.
- LARSON, A. C. & CROMER, D. T. (1961). *Acta Cryst.* **14**, 128.
- VÖLLENKE, H. & WITTMANN, A. (1971). *mh. Chem.* **102**, 1245.
- X-ray Handbook* (1965). Departments of Chemistry at the Univ. of Washington and Univ. of Maryland.

Acta Cryst. (1972). **B28**, 2838

The Crystal Structure of a Seco Steroid

BY C. S. YOO, J. PLETCHER AND M. SAX

The Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A.

and

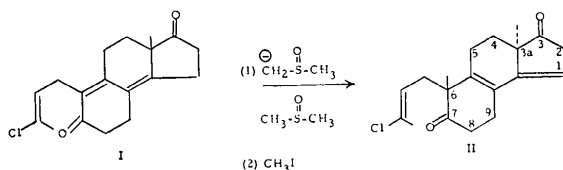
The Biocrystallography Laboratory, Veterans Administration Hospital, Pittsburgh, Pa. 15240, U.S.A.

(Received 28 October 1971 and in revised form 8 May 1972)

The crystal and molecular structure of *d,l*-3a,6-dimethyl-6-(*trans*-3-chlorobut-2-ene-1-yl)-2,4,5,6,8,9-hexahydro-3*H*-benz[e]indene-3,7-(3a*H*)-dione ($C_{19}H_{23}O_2Cl$), II, has been determined from X-ray diffraction data in order to establish the geometrical isomerism of the molecule. The space group is monoclinic, $P2_1/c$, with four molecules in a unit cell of dimensions: $a=10.091$ (3), $b=11.515$ (3), $c=14.709$ (4) Å, $\beta=92.54$ (4)°. The intensities of 2912 reflections were measured on a four-circle automated diffractometer using Cu $K\alpha$ radiation. The structure was refined by the anisotropic least-squares method to a final R value on F of 0.081 computed with all of the structure factor data. The results of the crystal structure analysis show that two methyl groups are in the *trans* configuration. The conjugated double bond in the fused ring system confers an approximately coplanar arrangement on nine of the thirteen atoms in the rings.

Introduction

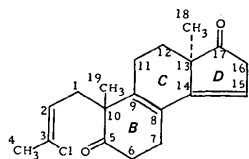
Compound II was prepared *via* base-induced methylation of dione I (Danishefsky *et al.*, 1972).



The relative stereochemical arrangement of the methyl groups at carbons (3a) and (6) was crucial to the possibility of subsequent use of II in the elaboration of steroids. The crystal structure of II was examined in order to determine whether these methyl groups are *cis* or *trans* with respect to the plane of the fused rings. This, in turn, had further significance with respect to the problem of the stereochemistry of methylation of extended enolates derived from dienones such as I. Another reason for examining the three-dimensional structure of II was the possibility of assessing the con-

formational effects of the 8,14-diene systems on the steroid system (for convenience in comparing this structure with other steroids, the conventional steroid numbering scheme in Table 1 will be adopted in the subsequent discussion).

Table 1. *Crystal data for seco steroid, C₁₉H₂₃O₂Cl*



C₁₉H₂₃O₂Cl M.W. = 318.847 m.p. = 132.5–133.5°C

Monoclinic, space group *P2₁/c* from systematic absences: *h0l* absent for *l* odd; *0k0* absent for *k* odd.

| | | |
|---|---|--|
| <i>a</i> = 10.091 (3) Å | } measured at 24°C | $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ |
| <i>b</i> = 11.515 (3) | | $\lambda(\text{Cu } K\alpha_1) = 1.54051$ |
| <i>c</i> = 14.709 (4) | | $\lambda(\text{Cu } K\alpha_2) = 1.5443$ |
| $\beta = 92.54 (4)^\circ$ | | $\mu(\text{Cu } K\alpha) = 20.17 \text{ cm}^{-1}$ |
| <i>V</i> = 1707.5 Å ³ | | <i>F</i> (000) = 680 |
| <i>Z</i> = 4 | | |
| <i>d_x</i> = 1.240 g.cm ⁻³ | | |
| <i>d_m</i> = 1.237 g.cm ⁻³ | measured by flotation method in aqueous potassium iodide solution at 23°C | |

Experimental

The crystals of II, which were supplied by Professor S. Danishefsky and Dr P. Solomon, are colorless, acicular in habit, and elongated in the direction of the unique axis. The space group was determined from oscillation and Weissenberg photographs. The unit-cell dimensions were deduced from manual 2θ scans of the observable axial reflections using a Picker automatic diffractometer equipped with a scintillation counter. The crystal was mounted such that its *b* axis coincided with the ϕ axis of the full-circle crystal orienter. Ni-filtered Cu $K\alpha$ radiation was used throughout the analysis. Table 1 contains the crystal data.

The integrated intensity measurements were made by scanning reflections in the $\theta:2\theta$ mode at a rate of 2°/min over a 2θ range of 2°. At both limits of this range, stationary 10 sec background counts were taken. Seven reflections were chosen as standards, and at least a pair of these were monitored at intervals of approximately two hours. Examination of the standards during the data collection revealed a gradual decrease of 7% in the diffraction intensity. Scale factors based on the seven standards compensate to a large extent for the time-dependent decrease.

In total, 2912 reflections were collected; of these 728 were less than $3\sigma(I)$, where $\sigma(I)$ is given by

$$\text{ATN}[(10S + 5) + 9\{(10B_1 + 5) + (10B_2 + 5)\}]^{1/2},$$

S is the total number of decacounts accumulated during the scan, and ATN is the attenuator factor. *B*₁ and *B*₂ are the accumulated background in decacounts. The intensities were corrected in the usual manner by the Lorentz and polarization factors, but they were not corrected for absorption.

Structure determination and refinement

An initial set of structure amplitudes ($|F_o|$) were calculated from the 2912 independent reflections. The X-ray 70 system of programs (Stewart, Kundell & Baldwin, 1970) was used to compute both a scale and an overall temperature factor from a Wilson (1942) plot, to convert the observed structure factor amplitudes to normal *E* values, and to determine the signs of 332 reflections, $E \geq 1.50$, by the direct method (programs *SIGMA 2* and *PHASE*). The coordinates of 17 atoms were obtained readily from an *E* map computed with the 332 normalized structure factors. The remaining 5 atoms, exclusive of the hydrogens, were located in a difference Fourier synthesis which followed a single cycle of isotropic full-matrix least-squares refinement of the partial structure. The parameters of the 22 atoms were then refined anisotropically by the full-matrix least-squares method. The Hughes (1941) weighting scheme was employed with $\sigma = F/11.3$ if $F > 11.3$ and with $\sigma = 1$ if $F \leq 11.3$. The function minimized was $\sum w(|F_o| - K|F_c|)^2$ where *K* is a single scale factor. Atomic scattering factors for chlorine, oxygen, and carbon were taken from the *International Tables for X-ray Crystallography* (1962), while those for hydrogen were taken from Stewart, Davidson & Simpson (1965). The hydrogen coordinates were obtained from a difference synthesis calculated when the *R* value had been reduced to 0.12 for all reflections. These were included as variables in subsequent cycles of refinement. However, hydrogen thermal parameters were not refined but were set equal to those of the atoms to which the hydrogens are bonded. The final reliability index was 0.081 for all 2912 independent reflections and 0.064 for the 2184 observed reflections. The structure amplitudes of all reflections are listed in Table 2. The atomic coordinates and thermal parameters with their e.s.d.'s are given in Table 3.

Other computer programs used in this analysis are the Shiono (1965) version of *ORFLS* (Busing, Martin & Levy, 1962), a modification of the Zalkin Fourier Synthesis (Shiono, 1967), the *ORTEP* program (Johnson, 1965), and a number of those listed in the University of Pittsburgh Crystallography Laboratory Technical Reports (Shiono, 1963–1968).

Discussion of the structure

The molecular shape and the thermal ellipsoids of the atoms are depicted in Fig. 1. The least-squares planes through some regions of the *B*, *C* and *D* rings and the distances of various atoms from these planes are given in Table 4. Planes 1 and 2 show that the conventional chair or boat description does not apply to the six-membered rings, *B* and *C*, because of the presence of unsaturation at C(8)–C(9). Ring *D* has a distorted envelope conformation as indicated by plane 3 and by torsion angle C(13)–C(14)–C(15)–C(16) which is 4.2°. As expected for a conjugated diene system, atoms C(7), C(8), C(9), C(10), C(11), C(13), C(14)

Table 2. Observed and calculated structure factors

The columns within each group in order from left to right are the running index $h, 10|F_o|$ and $10|F_c|$. Asterisks indicate unobserved reflections.

Table with multiple columns containing numerical data for observed and calculated structure factors. The table is organized into groups of columns, with some cells containing asterisks to denote unobserved reflections. The data includes values for h, 10|F_o|, and 10|F_c| across various indices.

Table 2 (cont.)

Table of atomic coordinates and thermal parameters for C1 through C19, O1, and O2. The table lists fractional coordinates x, y, z and thermal parameters β_{11} , β_{22} , β_{33} , β_{12} , β_{13} , β_{23} .

Table 3 (cont.)

Fractional coordinates × 10³

Table of fractional coordinates for atoms H1(C1) through H3(C19). Columns represent x, y, and z coordinates.

C(15) and C(16) are approximately coplanar, although significant deviations are apparent, especially in the cases of C(11), C(13) and C(16). If these atoms in plane 4 were strictly coplanar, then the B/C and C/D junctions would lie in a common plane, and torsion angle C(9)–C(8)–C(14)–C(15) would equal 180°. However, its observed value is 167°. Other torsion angles about the B/C and C/D junctions are listed in Table 5. Significantly, C(6) and C(12) are displaced in the same direction from plane 4. Therefore, rings B and C are in an extended boat conformation. CH₃(19) lies on the same side of plane 4 as C(6) and C(12) whereas the chlorobutanyl side chain and CH₃(18) lie on the oppo-

Table 3. Atomic parameters and their estimated standard deviations

Table with 8 columns: Cl, x, y, z, β_{11} , β_{22} , β_{33} , β_{12} , β_{13} , β_{23} . Lists thermal parameters for atoms C1 through O2.

site side. Accordingly, methyl groups $\text{CH}_3(18)$ and $\text{CH}_3(19)$ are in the *trans* configuration. The keto oxygen atom, O(1), lies -0.390 \AA out of plane 1 while the other keto oxygen, O(2), lies 0.886 \AA out of plane 3. The torsion angles around the C(1)–C(10) bond connecting the side chain are:

$\text{C}(2)\text{--C}(1)\text{--C}(10)\text{--C}(19) = -179.7^\circ$; $\text{C}(2)\text{--C}(1)\text{--C}(10)\text{--C}(5) = -65.8^\circ$; and $\text{C}(2)\text{--C}(1)\text{--C}(10)\text{--C}(9) = 58.4^\circ$. The Cl atom is *cis* relative to C(1).

The bond distances and valency angles with their associated standard deviations, exclusive of those involving hydrogen atoms, are shown in Fig. 2. The C–H bond distances lie in the range between 0.75 and 1.06 \AA . The single bonds to C(10) are longer than expected, even though the experimental bond distances in Fig. 2 are probably underestimated because of the thermal motion of the molecule. Bonds C(9)–C(10) and C(5)–C(10) exceed 1.505 \AA , the normally quoted

Table 4. *Some least-squares planes through groups of atoms*

Coefficients $\times 10^4$ in $Ax + By + Cz - D = 0$, referred to the crystallographic axes (x, y, z in \AA).

| Plane | No. | A | B | C | D |
|------------------------------|-----|-------|------|------|-------|
| C(7) C(8) C(9) C(10) | 1 | -1682 | 3775 | 9172 | 39721 |
| C(8) C(9) C(11) C(14) | 2 | -1459 | 3465 | 9322 | 40957 |
| C(13) C(14) C(15) C(16) | 3 | -2197 | 5224 | 8329 | 31629 |
| C(7) to C(16), C(12) omitted | 4 | -1662 | 4082 | 9041 | 39178 |

| Plane No. | Displacement from the plane ($\text{\AA} \times 10^3$) |
|-----------|---|
| 1 | C(7) 11, C(8) -24, C(9) 24, C(10) -11, C(5) 47, C(6) 698, O(1) -390. |
| 2 | C(8) 4, C(9) -4, C(11) 2, C(14) -2, C(12) 478, C(13) -218 |
| 3 | C(13) -12, C(14) 22, C(15) -22, C(16) 12, C(17) 370, O(2) 886 |
| 4 | C(7) -46, C(8) -37, C(9) 50, C(10) 20, C(11) 124, C(13) -233, C(14) -83, C(15) 66, C(16) 140, Cl -3542, C(1) -1239, C(2) -2507, C(3) -3528, C(4) -4747, C(5) 32, C(6) 646, C(12) 555, C(17) 300, C(18) -1708, C(19) 1278, O(1) -409, O(2) 780 |

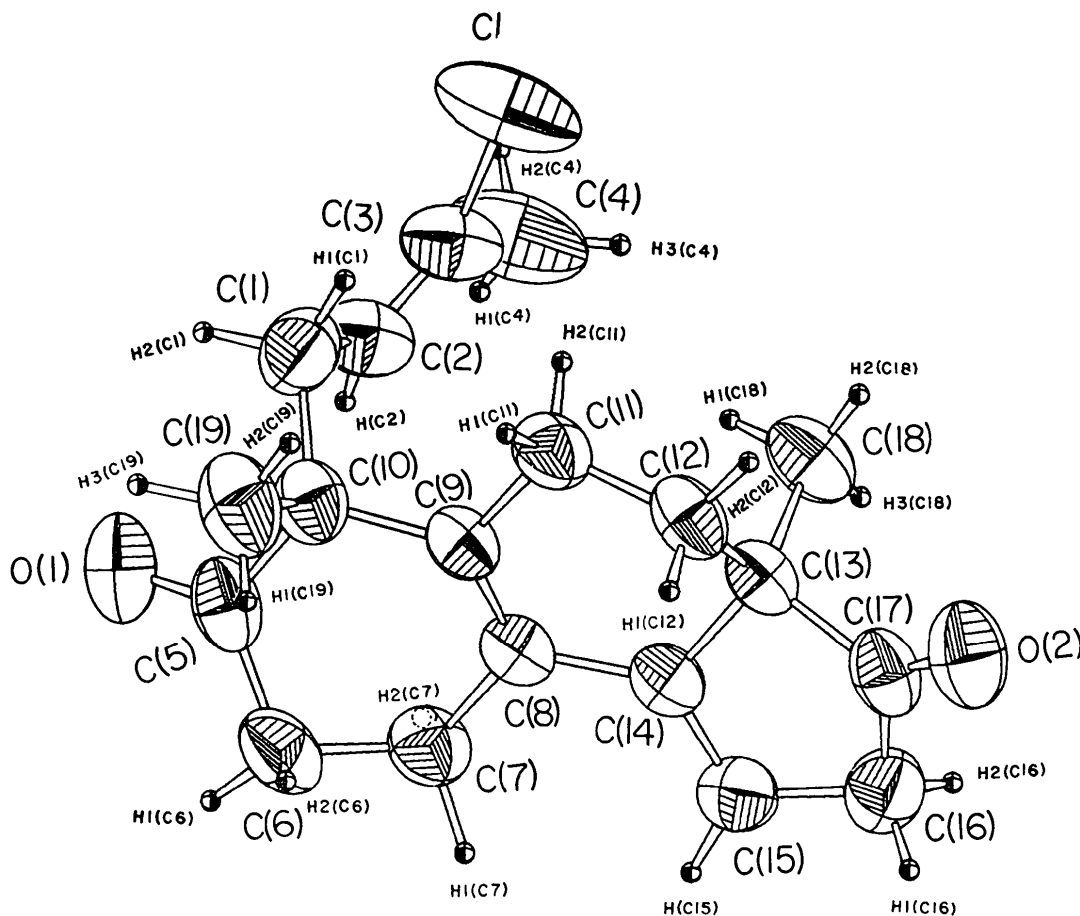


Fig. 1. A thermal ellipsoid plot (Johnson, 1965), at the 50% probability level, of one molecule showing the numbering system of the atoms.

distance for an sp^2-sp^3 single bond between carbon atoms (Bartell & Bonham, 1960) by 2.8 and 4.8σ respectively. Bonds C(1)–C(10) and C(19)–C(10) are 1.8

and 1.6σ greater than 1.54 Å, the sp^3-sp^3 distance. On the other hand, endocyclic bonds C(15)–C(16), C(16)–C(17), C(12)–C(13), C(11)–C(12), C(5)–C(6) and C(6)–

Table 5. Torsion angles in the rings and at the B/C and C/D junctions

Φ in Part I is the torsion angle about the specified bond. The other two atoms required to define the angle are attached to the ends of the bond and are in the ring in question.

The sign convention for the torsion angle is that of Klyne & Prelog (1960). The torsion angles in the other enantiomorph are opposite in sign.

Part I

| B ring | | C ring | | D ring | |
|------------|---------------|-------------|---------|-------------|---------|
| | Φ | | Φ | | Φ |
| C(5)–C(6) | -55.4° | C(9)–C(11) | -19.6 | C(13)–C(14) | -17.5 |
| C(6)–C(7) | 53.8 | C(11)–C(12) | 47.8 | C(14)–C(15) | 4.2 |
| C(7)–C(8) | -25.3 | C(12)–C(13) | -55.3 | C(15)–C(16) | 11.4 |
| C(8)–C(9) | -5.7 | C(13)–C(14) | 37.4 | C(16)–C(17) | -22.4 |
| C(9)–C(10) | 6.2 | C(14)–C(8) | -8.9 | C(17)–C(13) | 24.3 |
| C(10)–C(5) | 25.5 | C(8)–C(9) | -0.8 | | |

Part II

| B/C junction | | C/D junction | |
|------------------------|---------------|-------------------------|----------|
| | Φ | | Φ |
| C(7)–C(8)–C(9)–C(11) | 177.1° | C(8)–C(14)–C(13)–C(17) | 159.0 |
| C(10)–C(9)–C(8)–C(14) | 176.4 | C(12)–C(13)–C(14)–C(15) | -139.2 |
| C(6)–C(7)–C(8)–C(14) | 152.7 | C(8)–C(14)–C(15)–C(16) | -171.9 |
| C(5)–C(10)–C(9)–C(11) | -176.5 | C(12)–C(13)–C(17)–C(16) | 142.2 |
| C(7)–C(8)–C(14)–C(13) | 173.1 | C(11)–C(12)–C(13)–C(17) | -167.8 |
| C(10)–C(9)–C(11)–C(12) | 163.0 | | |

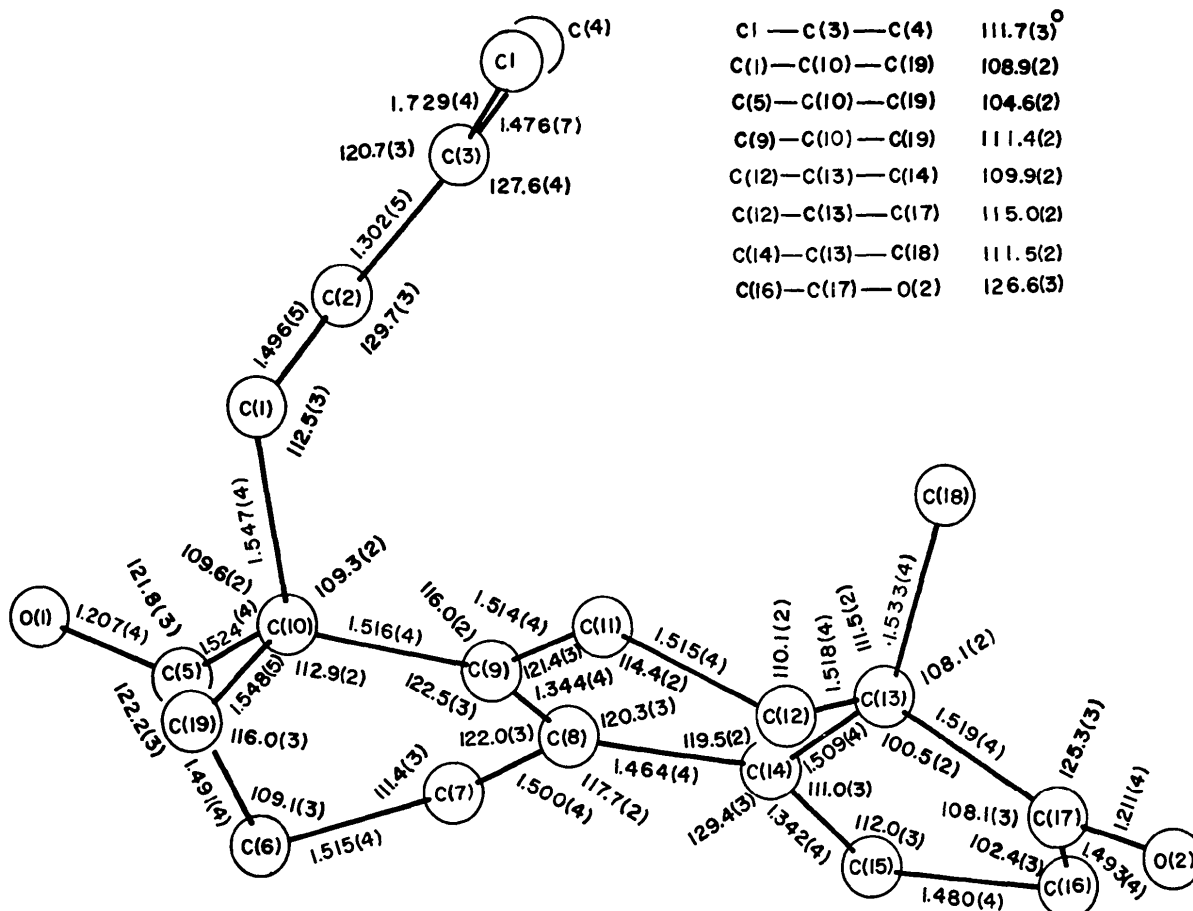


Fig. 2. Interatomic distances (Å) and angles ($^\circ$) for the molecule. The estimated standard deviations are given in parentheses following the listed values.

C(7) are shorter by 6.3, 3.0, 5.5, 6.3, 3.5 and 6.3 σ respectively, than their expectation values. Bonds C(2)–C(3) and C(3)–C(4) in the chlorobutenyl side chain are fore-shortened by 6.8 and 4.1 σ , seemingly due to thermal disorder.

The projections of the structure along the *b* and *c* axes, illustrating the packing of the molecules, are shown in Figs. 3 and 4. The intermolecular contacts between nonhydrogen atoms which are less than 4 Å are listed in Table 6. The distances between neighboring molecules correspond to normal van der Waals interactions.

Table 6. Intermolecular distances less than 4 Å between nonhydrogen atoms

| | |
|-------------|---------|
| C(1)–C(6') | 3.967 Å |
| C(11)–O(1') | 3.964 |
| C(12)–Cl'' | 3.987 |
| C(19)–O(1') | 3.441 |
| C(19)–C(5') | 3.950 |
| C(19)–Cl'' | 3.971 |

Symmetry code:

| | |
|----|------------------------------------|
| ' | $-x, \frac{1}{2}+y, \frac{1}{2}-z$ |
| '' | $x, \frac{1}{2}-y, \frac{1}{2}+z$ |

This research was supported by the U.S. Public Health Service, National Institutes of Health, under Grant No. NS-09178-07. The computing facilities of the Department of Crystallography and the Computer Center of the University of Pittsburgh were used throughout this research.

We gratefully acknowledge the assistance of Professor S. Danishefsky with this research.

References

- BARTELL, L. S. & BONHAM, R. A. J. (1960). *J. Chem. Phys.* **32**, 824.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*, Report ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- DANISHEFSKY, S., SOLOMON, P., CRAWLEY, L. S., SAX, M., YOO, C. S., ABOLA, E. & PLETCHER, J. (1972). *Tetrahedron Letters*, **10**, 961.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **65**, 1737.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KLYNE, W. & PRELOG, D. (1960). *Experientia*, **16**, 521.
- SHIONO, R. (1965). A Modification of *ORFLS* for the Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pa.
- SHIONO, R. (1967). A Modification of the Zalkin Fourier Synthesis Program, Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pa.
- SHIONO, R. (1963–1968). Technical Reports TR-63-2, 3, 4, TR-68-1, 2. Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). *X-ray 70 System of Crystallographic Programs*, Computer Science Center, University of Maryland, College Park, Md.

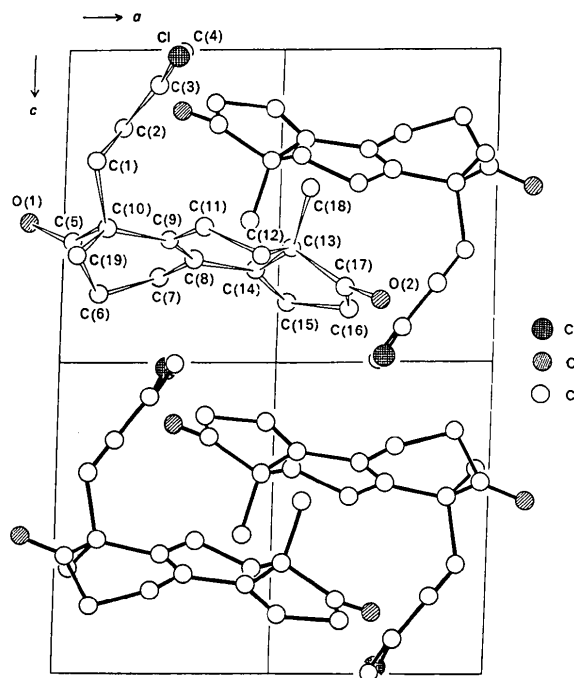


Fig. 3. Projection of one unit cell along the *b* axis.

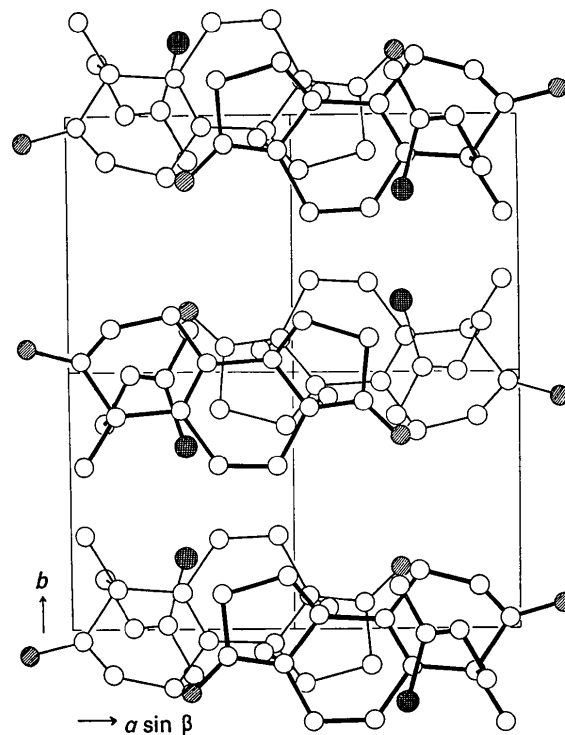


Fig. 4. Projection of one unit cell along the *c* axis.

- STEWART, R. F., DAVIDSON, R. E. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.