The intermolecular contacts less than 3·8 Å between pairs of non-hydrogen atoms are listed in Table 10. Some short C···O contacts are observed. [The normal van der Waals separation between a methyl carbon and an oxygen atom is 3·40 Å (Pauling, 1960).]
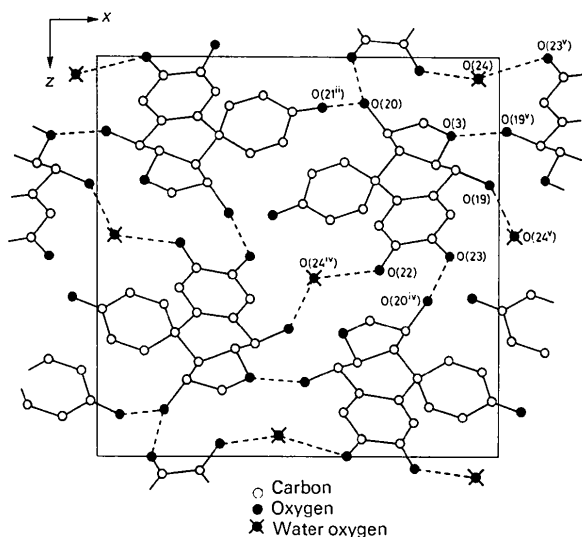
Fig. 3. The structure as seen in projection down the *b* axis.

○ Carbon
● Oxygen
✖ Water oxygen
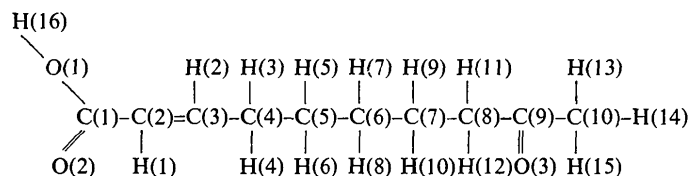
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The Crystal Structure of Queen Substance, 9-Keto-*trans*-2-decenoic Acid, the Sex Pheromone of the Honeybee*

By DON T. CROMER AND ALLEN C. LARSON

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, U.S.A.

The structure of 'queen substance', 9-keto-*trans*-2-decenoic acid, the sex pheromone of the honeybee, has been determined. The crystals are monoclinic, space group $P2_1/c$ with $a = 9\cdot584$ (9), $b = 8\cdot642$ (7), $c = 13\cdot371$ (12) Å, $\beta = 96° 58$ (4)′, and $Z = 4$. Intensities were measured with an automated diffractometer, using graphite monochromated Mo $K\alpha$ radiation. The structure was solved by the symbolic addition method. The atoms have unusually large anisotropic thermal parameters and possibly a small amount of disorder caused by occasional reversal of molecules. Bond length corrections are needed, because of the large thermal parameters, but could not be made for lack of a suitable model of correlated motion.

Introduction

Insect pheromones, or sex attractants, are an important class of biologically active substances currently

receiving intensive study. Most known pheromones are liquids at room temperature and thus are not easily studied by X-ray crystallography. The pheromone of the honeybee, 9-keto-*trans*-2-decenoic acid, however, is a solid at room temperature, and we have now determined its crystal structure. This compound is commonly referred to as 'queen substance'. The structural

formula with the numbering scheme used in this paper is shown below.

$(\lambda = 0.70926$ Å$)$, measured on an automated Picker diffractometer (Busing & Levy, 1967).

H(16)
\
   O(1)   H(2) H(3) H(5) H(7) H(9) H(11)   H(13)
    \ | | | | | | |
C(1)-C(2)=C(3)-C(4)-C(5)-C(6)-C(7)-C(8)-C(9)-C(10)-H(14)
 // | | | | | | || |
O(2)   H(1)   H(4) H(6) H(8) H(10)H(12)O(3) H(15)

One aspect of the theory of the action of insect attractants is that the molecule fits neatly into a receptor site (Klopping & Meade, 1971). Hence, a detailed knowledge of the size and shape of the molecule is of considerable interest. Unfortunately in the present case, because of extreme thermal motion or because of disorder in the crystal, the interatomic distances could not be determined with much certainty.

Queen substance is a sex attractant for drone honeybees, and also has other regulatory functions. It is remarkably specific. Blum, Boch, Doolittle, Tribble & Traynham (1971) have studied 19 closely related alkenoic acids and found that none of these functions as an attractant.

Experimental

Synthetic material was kindly provided by Dr Murray Blum of the entomology department of the University of Georgia. Suitable crystals were grown from solution in n-hexane. The compound is monoclinic, space group $P2_1/c$ with $a = 9.584$ (9), $b = 8.642$ (7), $c = 13.371$ (12) Å, $\beta = 96°58$ (4)', and $Z = 4$. The calculated density is 1.13 g.cm^{-3}. Systematic extinctions observed were $0k0$ absent when $k = 2n + 1$, and $h0l$ absent when $l = 2n + 1$. Lattice constants were determined from a least-squares analysis of 12 reflections

Intensities were measured with the automated Picker diffractometer, using local versions of the orientation, least-squares, and data-collection programs of Busing, Ellison, Levy, King & Roseberry (1968). A θ–2θ scan technique was used with steps of $0.05°$ over a $2°$ 2θ range and a 2 sec count at each step. Background was counted for 20 sec at each end of the range and was assumed to vary linearly within the range. Graphite monochromated Mo $K\alpha$ radiation was used. Reflections for $h \geq 0$, and all values of k and l were measured to a maximum 2θ of $45°$. 3320 reflections were measured. Reflections were considered observed if $I - B \geq 2\sigma(I) = [I + B + (kI)^2]^{1/2}$, where I is the total count, B the background count, and $k = 0.015$ is an instrumental constant. Equivalent reflections were averaged, and 855 unique reflections were observed out of a possible 1449. Weights of the structure factors were derived from $\sigma(I)$ (Stout & Jensen, 1968). A disagreement index for the averaged reflections, defined as $R_F = \sum_n \sum_i |\bar{F} - F_{i,n}| / \sum_n \sum_i F_{i,n}$, was 0.023, where $\bar{F} = \sum_i w_i F_i /$ $\sum w_i$. The w_i's are the weights of the F_i's, and the summation is over all n sets of i equivalent F_i. The crystal used was approximately a parallelepiped, measuring $0.1 \times 0.1 \times 0.2$ mm. No absorption corrections were made or considered necessary.

During the data collection, the intensity of a standard reflection decreased by about 15%. Individual reflections were corrected for this loss by the fitting of a quadratic function of time to the standard reflection intensity. At least part of the loss was due to sublimation of the crystal.

Determination and refinement of the structure

A Wilson plot showed a large average isotropic thermal parameter $(B \simeq 8$ Å$^2)$. Intensities were scaled and converted to E's for application of the symbolic addition method. The structure was eventually solved by this direct method, but only after a great many trials. In retrospect, the source of the difficulty was the large anisotropic thermal motion. It was difficult to recognize the molecule, and the correct heavy-atom structure refined poorly with isotropic thermal parameters. In the E map from which the structure was finally deduced, about 10% of the signs were wrong. Later, an anisotropic thermal correction was applied in the computation of the E's; the symbolic addition method then proceeded smoothly to the solution.
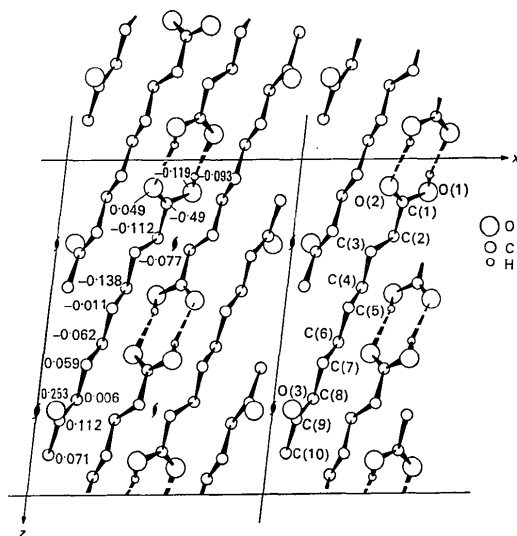

Fig. 1. View of the structure looking down the b axis. Numbers adjacent to some atoms are the y coordinates.

Hindsight suggests that a large B from a Wilson plot is a warning of trouble ahead.

Refinement was made by full-matrix least-squares methods, which minimized $\sum w(F_o - KF_c)^2$, where K is a scale factor. R indices quoted are $R = \sum |\Delta F|/\sum |F_o|$ and $R_w = [\sum w |\Delta F|^2/\sum w F_o^2]^{1/2}$, with unobserved reflections omitted. The scattering factor for oxygen was taken from Doyle & Turner (1968); that for hydrogen from Stewart, Davidson & Simpson (1965); and that for carbon from a valence state Hartree–Fock value (Cromer, 1968). Trivial anomalous dispersion terms were formally included (Cromer & Liberman, 1970).

The heavy-atom structure, with individual isotropic thermal parameters, refined to $R = 0.25$. When anisotropic thermal parameters were added, R was reduced to 0.17. Bond lengths were rather abnormal, with some C–C distances being as long as 1.62 Å, and the double bond was 1.1 Å. Thermal parameters were large and very anisotropic.

The model was then constrained to assume normal bond lengths and bond angles (Rollett, 1970), and R was reduced to 0.12. A false minimum had been found in the earlier refinements. The positions of the heavy atoms in the false minimum were not far from those in the final model, and it is surprising that better convergence was not achieved at that time. The range of

differences was 0.032 to 0.145 Å, with a mean of 0.081 Å.

Hydrogen atoms were then added in positions calculated from normal geometry and with isotropic thermal parameters held constant at 10 Å². With all distances constrained, R was reduced to 0.106 and R_w to 0.097. For the final refinement, all distance constraints were removed, and the hydrogen thermal parameters were held constant at the value of the anisotropic parameters of the atom to which they were bonded, plus an isotropic parameter of 1 Å². This refinement gave $R = 0.087$ and $R_w = 0.053$. The hydrogen atoms remained in reasonable positions, except for H(1) and H(2) on the atoms forming the double bond.

The final parameters are given in Table 1, and the observed and calculated structure factors are listed in Table 2.

Discussion

A drawing of the structure is shown in Fig. 1. As is typical for carboxylic acids, two carboxylic groups face each other at a center of symmetry. A stereoview of a single molecule, showing the thermal ellipsoids, is given in Fig. 2. The thermal ellipsoid axes range from 3 to 25 Å². The bond distances and angles for

Table 1. *Final least-squares parameters for 9-keto-trans-2-decenoic acid*

Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. Hydrogen thermal parameters are 1.0 Å² plus that of the bonded atom.

	x	y	z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
O(1)	0.5498 (6)	−0.1193 (5)	0.0981 (3)	439 (10)	425 (11)	75 (3)	129 (16)	82 (11)	104 (9)
O(2)	0.3808 (5)	0.0489 (6)	0.0806 (3)	343 (10)	518 (13)	98 (4)	274 (16)	107 (8)	30 (10)
O(3)	0.0802 (5)	0.2526 (5)	0.7482 (3)	547 (11)	285 (8)	194 (4)	322 (17)	274 (11)	89 (10)
C(1)	0.4480 (8)	−0.0487 (9)	0.1279 (5)	253 (15)	418 (20)	73 (6)	−194 (28)	153 (14)	−107 (15)
C(2)	0.4318 (16)	−0.1119 (17)	0.2318 (6)	403 (19)	591 (34)	99 (7)	−465 (35)	169 (22)	−135 (24)
C(3)	0.3370 (13)	−0.0768 (14)	0.2754 (8)	486 (22)	529 (31)	107 (7)	−469 (42)	192 (26)	−156 (24)
C(4)	0.3188 (9)	−0.1378 (9)	0.3818 (5)	531 (23)	413 (20)	84 (6)	−309 (30)	224 (18)	−41 (16)
C(5)	0.2728 (6)	−0.0105 (7)	0.4425 (4)	273 (13)	344 (13)	75 (5)	−101 (20)	54 (13)	52 (13)
C(6)	0.2465 (5)	−0.0623 (7)	0.5474 (4)	297 (13)	284 (12)	71 (4)	−96 (22)	89 (12)	9 (13)
C(7)	0.1897 (6)	0.0592 (7)	0.6086 (4)	246 (11)	254 (12)	92 (5)	15 (19)	65 (11)	74 (13)
C(8)	0.1672 (6)	0.0063 (6)	0.7126 (4)	221 (11)	224 (11)	85 (4)	−14 (16)	75 (11)	−9 (11)
C(9)	0.1023 (6)	0.1216 (7)	0.7748 (4)	239 (10)	250 (12)	116 (5)	59 (19)	81 (11)	22 (14)
C(10)	0.0700 (9)	0.0706 (8)	0.8769 (6)	374 (16)	313 (17)	129 (6)	65 (25)	197 (16)	−41 (17)

Table 1 (*cont.*)

	x	y	z	Bonded atom
H(1)	0.432 (11)	−0.169 (9)	0.276 (6)	C(2)
H(2)	0.349 (10)	0.007 (7)	0.241 (5)	C(3)
H(3)	0.400 (7)	−0.197 (7)	0.409 (4)	C(4)
H(4)	0.234 (5)	−0.223 (5)	0.370 (3)	C(4)
H(5)	0.357 (6)	0.053 (5)	0.446 (3)	C(5)
H(6)	0.180 (5)	0.023 (5)	0.407 (3)	C(5)
H(7)	0.335 (5)	−0.096 (5)	0.577 (3)	C(6)
H(8)	0.175 (5)	−0.161 (4)	0.537 (3)	C(6)
H(9)	0.247 (4)	0.163 (4)	0.610 (3)	C(7)
H(10)	0.102 (4)	0.095 (5)	0.572 (3)	C(7)
H(11)	0.100 (4)	−0.078 (4)	0.705 (3)	C(8)
H(12)	0.261 (4)	−0.018 (4)	0.752 (3)	C(8)
H(13)	0.012 (6)	−0.017 (5)	0.869 (4)	C(10)
H(14)	0.139 (6)	0.009 (6)	0.908 (4)	C(10)
H(15)	0.040 (6)	0.157 (5)	0.904 (3)	C(10)
H(16)	0.550 (7)	−0.093 (7)	0.048 (3)	O(1)

carbon and oxygen atoms are in Table 3. The O(1)–H(16) bond is 0.71 Å, and the C–H bonds range from 0.77 to 1.09 Å.

In order for the substance to dissipate in its natural environment, it must have an appreciable vapor pressure, and large thermal motion might therefore be expected. The thermal motion, however, is rather larger than that found in somewhat related compounds. For example, the average B is about 5 Å² in DL-2-methyl-7-oxododecenoic acid (O'Connell, 1968) and in decanamide (Brathovde & Lingafelter, 1958).

It is possible that some disorder is present in the crystal. The keto group on C(9) gives the same shape to both ends of the molecule, and as the crystal grows an occasional molecule may be reversed. Indeed, an inspection of Fig. 1 shows how this faulting might

happen. Invert, through the symmetry center at $\frac{1}{2}0\frac{1}{2}$, the molecule labeled with the y coordinates. By a translation of $x \simeq -\frac{1}{2}$, the 10-carbon chain almost superimposes on the original chain. With a little twisting at the ends, it appears that the molecule ought to fit backwards into the unit cell without great

Table 2. *Observed and calculated structure factors for 9-keto-trans-2-decenoic acid*

Column headings are l, $10F_o/K$, $10F_c$, and $10\sigma(F_o/K)$. A minus sign preceding F_o means 'less than', and the value listed is that derived from $2\sigma(l)$.
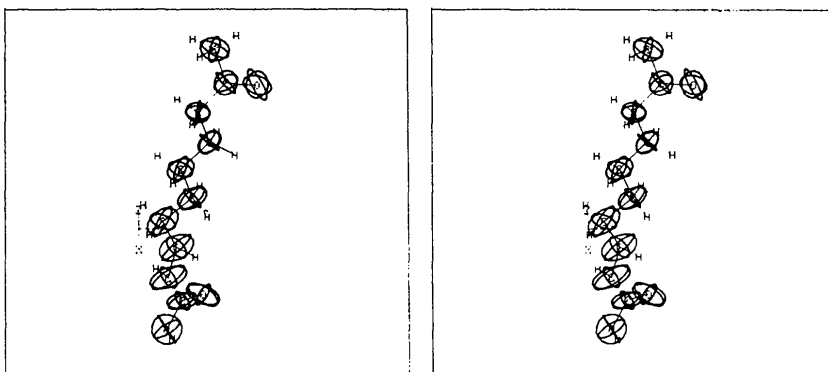

Fig. 2. Stereoview of the molecule, showing thermal ellipsoids. The axes of the ellipsoids are scaled to three times the r.m.s. amplitudes.

Table 3. *Interatomic distances and bond angles in 9-keto-trans-2-decenoic acid, uncorrected for thermal motion*

Standard deviations, in parentheses, are derived from the inverse least-squares matrix and are only formal values

O(1)–O(2)	2·168 (7) Å²	O(1)—C(1)–O(2)	124 (1)°
O(1)–O(2')	2·628 (7)	O(1)—C(1)–C(2)	107 (1)
C(1)–O(1)	1·256 (7)	O(2)—C(1)–C(2)	129 (1)
C(1)–O(2)	1·195 (7)	C(1)—C(2)–C(3)	122 (2)
C(1)–C(2)	1·517 (11)	C(2)—C(3)–C(4)	123 (2)
C(2)–C(3)	1·177 (16)	C(3)—C(4)–C(5)	109 (1)
C(3)–C(4)	1·548 (13)	C(4)—C(5)–C(6)	113 (1)
C(4)–C(5)	1·466 (9)	C(5)—C(6)–C(7)	115 (1)
C(5)–C(6)	1·522 (6)	C(6)—C(7)–C(8)	114 (1)
C(6)–C(7)	1·475 (7)	C(7)—C(8)–C(9)	116 (1)
C(7)–C(8)	1·504 (6)	C(8)—C(9)–C(10)	117 (1)
C(8)–C(9)	1·482 (7)	C(8)—C(9)–O(3)	123 (1)
C(9)–C(10)	1·503 (8)	C(10)–C(9)–O(3)	120 (1)
C(9)–C(3)	1·198 (5)		

difficulty. This disorder is by no means complete, but even a few misoriented molecules could distort the thermal parameters.

With the exception of C(3)–C(4), the bond lengths given in Table 3 are shorter than expected. The most extreme case is that of C(2)–C(3), the double bond, which is about 0·14 Å shorter than the usual value of 1·32 Å. C(1)–O(2) and C(9)–O(3) are short by about 0·08 Å, and the remaining C–C bonds are from 0·02 to 0·07 Å shorter than usual. These distortions surely arise from the large anisotropic thermal parameters. The lower-limit corrections (Johnson, 1970) are far too small, the largest being 0·015 Å for the C(1)–O(2) and the C(9)–O(3) distances. All other lower-limit corrections are less than 0·006 Å. A riding model does not seem physically applicable to any of the individual bonds in the present case. Treating the whole molecule as a rigid body, a dubious model for a long-chain compound, gives a maximum correction of 0·02 Å. We can conclude only that the standard deviations listed in Table 3 are grossly underestimated because of systematic error in our model. Lack of knowledge of the correlation of the thermal motion of neighboring atoms, prevents the bond lengths from being corrected. Any disorder present will only make the situation worse.

The hydrogen atoms, in general, refined to reasonable positions, except that H(1) is moved toward C(3) and H(2) is moved toward C(2), as shown in Fig. 2. A difference Fourier map of the final model showed peaks of 0·2 e.Å⁻³ on both sides of the double bond. H(1) and H(2) appear to have migrated toward these positions. Other peaks of about the same size are near C(1), C(2), and C(3), and near the oxygen atoms. All these features might well be associated with the pro-

posed disorder. An analysis at low temperature ought to show whether the thermal parameters are real or artifacts produced by disorder.

Blum *et al.* (1971) have calculated the minimum energy conformation of an isolated molecule of queen substance by the method of molecular mechanics (Allinger, Miller, Hirsh, Tyminski & Van Catledge, 1968). They found the entire molecule to be planar except for H(13), H(14), and the methylene hydrogen atoms on C(4) through C(8).

The observed conformation of the molecule in the solid is best described in terms of two planes rotated by 32°. Plane 1 contains atoms C(1), C(2), C(3), C(4), O(1), O(2), and H(16) with a maximum deviation of 0·04 Å. Plane 2 contains C(5) through C(10), O(3), H(15), and the maximum deviation is 0·06 Å. H(15) on the methyl group is in the eclipsing position with respect to the carbonyl oxygen O(3). A small bend in the molecule between C(4) and C(5) can be seen in Fig. 2.

Atoms C(1), C(2), C(3), and C(4) all lie within 0·004 Å from their least-squares plane. The angle of twist about the double bond is 45′.

All calculations were made on CDC-6600 and 7600 computers, using the Los Alamos system of crystal-structure programs.

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