

a communiqué les résultats concernant le calcul théorique de la molécule, et Mme Leroy pour sa contribution aux différents calculs nécessaires à la détermination de ces structures.

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Acta Cryst. (1973). **B29**, 313

The Crystal Structure of *cis*-9-Methyl-10-ethyl-9,10-dihydroanthracene

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(Received 22 September 1972; accepted 26 October 1972)

The crystal structure of *cis*-9-methyl-10-ethyl-9,10-dihydroanthracene, C₁₇H₁₈, has been determined by the application of direct methods. Three-dimensional data were collected on a Datex-automated General Electric diffractometer to a minimum spacing of 1.0 Å. The coordinates of all atoms in the molecule, the isotropic temperature factors for the hydrogen atoms, and the anisotropic temperature factors for the carbon atoms were refined by the method of least squares. The final *R* index is 0.031. The crystals are orthorhombic, space group *Pca*2₁, with *a* = 14.119 (3), *b* = 12.638 (3) and *c* = 7.290 (2) Å. The bond distances and angles are normal within experimental error.

Introduction

This compound, 9-methyl-10-ethyl-9,10-dihydroanthracene, C₁₇H₁₈, was obtained by Schaeffer & Zieger (1969) during a study of the stereochemistry of reactions of 9-alkyl-9,10-dihydroanthracenyllithiums. Spectral studies by these investigators and studies by Harvey, Arzadon, Grant & Urberg (1969) and Redford (1968) indicated that the molecule was in the *cis*-conformation at the 9,10 positions. This structure determination was undertaken to confirm this indication.

Experimental

The crystal used in this investigation was cut to a size of 0.2 × 0.2 × 0.3 mm from a larger crystal supplied by

Schaeffer and Zieger. Precession photographs of the crystal showed *mmm* symmetry and absence of *Ok**l* reflections with *l* odd and of *h*0*l* reflections with *h* odd, indicating that the space group is either *Pca*2₁ or *Pcam*. The unit-cell parameters were determined from measurements on precession photographs calibrated by lines diffracted from a powdered sample of NaCl (*a*₀ = 5.6402 Å). The resulting values for the unit-cell dimensions are:

$$\begin{aligned} a &= 14.119 (3) \text{ \AA} \\ b &= 12.638 (3) \\ c &= 7.290 (2). \end{aligned}$$

The density of the crystals measured by the flotation method is 1.116 g cm⁻³; and the density calculated, assuming four molecules per unit cell, is 1.135 g cm⁻³.

Intensity data were collected by the θ -2 θ scan method on a Datex-automated General Electric diffractometer using Ni-filtered Cu K α radiation. The scan speed was one degree in 2 θ per min and background counts of thirty sec were collected at both ends of the scan. All

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† Contribution No. 4555 from the Gates and Crellin Laboratories of Chemistry.

reflections to a minimum spacing of 1 Å were collected. These numbered 753, of which 7 were observed to have intensities not significantly greater than background and were assigned zero weight and were excluded from the R index. No correction for absorption was made ($\mu=4.8 \text{ cm}^{-1}$).

The data were placed on an approximate absolute scale by Wilson's (1942) statistical method. A Howells,

Phillips & Rogers (1950) plot indicated no center of symmetry, and hence space group $Pca2_1$.

Phase determination

A general description of the phase determination procedure has been given by Karle & Karle (1966). The normalized structure factors $|E|$ were calculated using

Table 1. Observed and calculated structure factors

Within each group the columns contain h , $10F_o$, $10F_c$, and ϕ_c ($^\circ$), the phase angle. Reflections marked with a negative F_o were assigned zero weight in the final least-squares cycles.

Table with multiple columns for h, 10Fo, 10Fc, phi_c, and other data points. The table is organized into groups and contains numerical values for each parameter.

Table 2. Carbon atom parameters and their standard deviations

The values have been multiplied by 10^5. The temperature factor is in the form

T = exp [- (b11h^2 + b22k^2 + b33l^2 + b12hk + b13hl + b23kl)] .

Table with columns for x, y, z, b11, b22, b33, b12, b13, b23 and rows for C(1) through C(17) with their corresponding coordinates and parameters.

an overall temperature parameter of 5.0 \AA^2 . The program used for phase determination in this investigation was written and kindly provided by Dr Ricardo Destro of the Istituto di Chimica Fisica dell'Università, Milano. The phases of three reflections were assigned to specify the origin in space group $Pca2_1$ (Hauptman & Karle, 1956); and one phase was assigned to specify the enantiomorph. These reflections were chosen on the basis of their large E values and the large number of relationships with other reflections with large E values. The reflections chosen were 221, 413, 512 and 5,11,0 and their assigned phases were $\pi/2$, $\pi/4$, $-\pi/4$ and 0 respectively. Through the application of the Σ_2 -relationship, it was possible to determine phases for nine additional reflections. These thirteen reflections were then used as a starting set for the application of the tangent formula (Karle & Haupt-

man, 1956). By the cyclic application of the tangent formula the phases of 122 reflections, with E values greater than 1.3, were eventually determined.

The reflections whose phases had been determined by the method described above were used to calculate an E map. Sixteen of the seventeen carbon atoms were readily located in this map; the position of the remaining carbon atom was determined from an electron-density map calculated on the basis of the known atoms.

Refinement of the structure

All calculations below were carried out on an IBM 360/75 computer with subprograms operating under the CRYM system [a modification of the CRYM system for the IBM 7094 computer (Duchamp, 1964)]. The atomic scattering factor for C was taken from *International Tables for X-ray Crystallography* (1962), and for H from Stewart, Davidson & Simpson (1965). The least-squares routine minimized the quantity $\sum w(F_o^2 - F_c^2)^2$. The weights, w , were set equal to $1/\sigma^2(F_o^2)$. The variance of the intensity was calculated by the formula:

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2,$$

where S is the total counts collected during the scan, B_1 and B_2 are the numbers of counts collected for each background, α is the ratio of scan time to total background time, and d is an empirical constant taken to be 0.02.

In space group $Pca2_1$, the location of the origin in the z direction is arbitrary. Accordingly, the z coordinate of atom C(10) was held constant throughout the refinement of the structure. After several cycles of refinement of the coordinates and anisotropic temperature factors of the carbon atoms, 12 hydrogen atoms were introduced at their expected positions. The remaining six hydrogen atoms – those of the methyl groups – were located on difference Fourier maps calculated in the planes of their expected positions. Both the coordinates and isotropic temperature factors for the hydrogen atoms were included in the subsequent refinement. In the later stages of refinement a second-

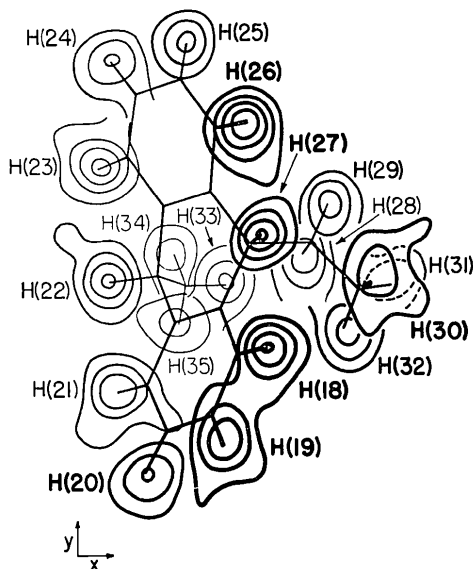


Fig. 1. A composite of sections of a three-dimensional difference electron-density map through each of the hydrogen atoms, viewed down the c axis. The lowest contour is at 0.1 e\AA^{-3} . The successive contours are at 0.2, 0.3, 0.4, ... e\AA^{-3} .

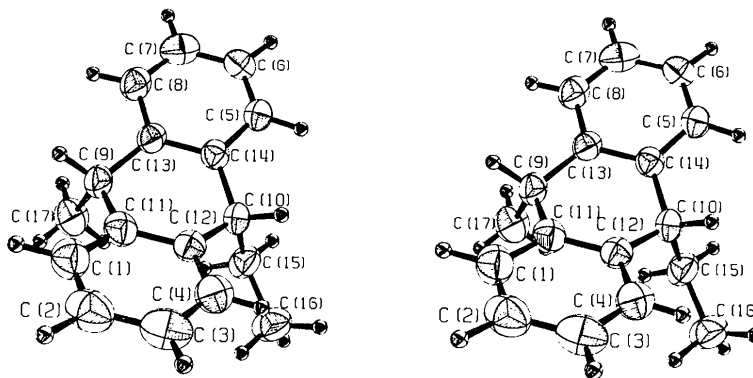


Fig. 2. Stereoscopic view of the molecule.

ary extinction factor was also included; the expression used is $F_{\text{corrected}}^2 = (F_{\text{cal}})^2 / [1 + g\beta(F_{\text{cal}})^2]$ (Larson, 1967). During the final cycles of refinement the coordinates for all atoms were contained in one matrix, and the temperature factors, scale factor, and secondary extinction factor were included in a second matrix. The final value obtained for the secondary extinction factor g is $23(\pm 1) \times 10^{-6}$. The final R index, $\sum |F_o| - |F_c| / \sum |F_o|$, is 0.031; the weighted R index, $\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4$, is 0.004; the 'goodness-of-fit', $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$ (where m is the number of observations and s is the number of parameters being refined), is 1.8.

Table 3. Hydrogen atom parameters and their standard deviations

The values for the coordinates have been multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(18)	5162 (17)	6235 (19)	6763 (41)	4.1 (0.7)
H(19)	4436 (18)	4618 (20)	6842 (45)	5.2 (0.8)
H(20)	3273 (18)	4144 (20)	4634 (51)	6.0 (0.8)
H(21)	2813 (16)	5443 (17)	2422 (48)	5.4 (0.8)
H(22)	2699 (17)	7281 (15)	1793 (37)	3.8 (0.6)
H(23)	2503 (23)	9117 (15)	1130 (45)	4.9 (0.7)
H(24)	2730 (17)	10911 (17)	1966 (43)	5.2 (0.8)
H(25)	3921 (17)	11309 (20)	4220 (40)	4.2 (0.7)
H(26)	4872 (19)	9939 (23)	5367 (41)	3.6 (0.6)
H(27)	5084 (18)	8090 (19)	5917 (39)	3.6 (0.6)
H(28)	5708 (19)	7703 (20)	2370 (54)	5.2 (0.8)
H(29)	6094 (17)	8657 (20)	3720 (39)	4.1 (0.7)
H(30)	6764 (28)	7257 (31)	5876 (78)	10.8 (1.2)
H(31)	7196 (23)	7342 (23)	3864 (61)	8.3 (1.0)
H(32)	6368 (17)	6384 (21)	4213 (46)	5.7 (0.8)
H(33)	4542 (20)	7312 (19)	211 (44)	4.7 (0.8)
H(34)	3622 (22)	7859 (23)	-788 (62)	8.1 (1.0)
H(35)	3745 (22)	6560 (27)	-254 (66)	8.4 (1.0)

The observed and calculated structure factors, F_o and F_c , and the phase angles, ϕ , are listed in Table 1.

The final coordinates and anisotropic temperature factors for the carbon atoms and their standard deviations, calculated from the least-squares residuals, are

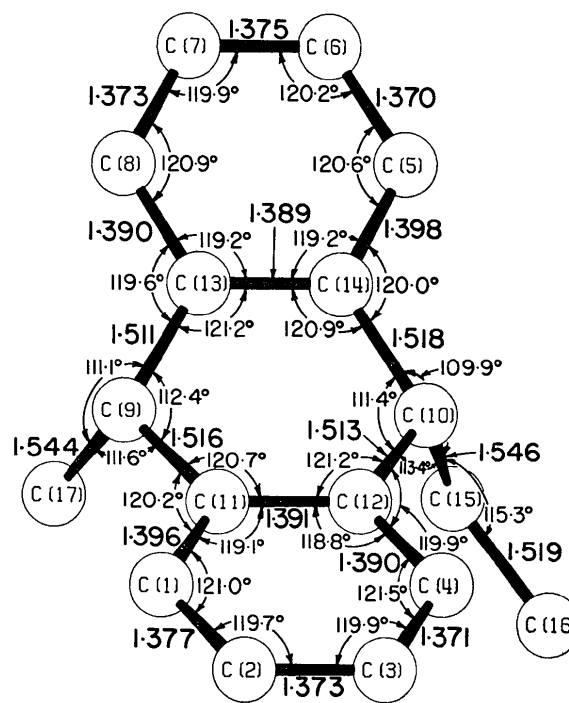


Fig. 3. Bond distances and angles for the carbon atoms of the molecule.

Table 4. Bond distances and angles involving hydrogen atoms

H(18)-C(4)	0.92 Å	H(18)-C(4)-C(3)	118°	H(27)-C(10)	0.99 Å	H(27)-C(10)-C(12)	107°
		H(18)-C(4)-C(12)	121			H(27)-C(10)-C(14)	110
						H(27)-C(10)-C(15)	105
H(19)-C(3)	0.93	H(19)-C(3)-C(2)	118	H(28)-C(15)	0.95	H(28)-C(15)-C(10)	106
		H(19)-C(3)-C(4)	122			H(28)-C(15)-C(16)	107
						H(28)-C(15)-H(29)	117
H(20)-C(2)	1.02	H(20)-C(2)-C(1)	116	H(29)-C(15)	0.98	H(29)-C(15)-C(10)	105
		H(20)-C(2)-C(3)	124			H(29)-C(15)-C(16)	108
H(21)-C(1)	1.04	H(21)-C(1)-C(2)	123	H(30)-C(16)	1.16	H(30)-C(16)-C(15)	116
		H(21)-C(1)-C(11)	116			H(30)-C(16)-H(31)	100
						H(30)-C(16)-H(32)	101
H(22)-C(9)	1.02	H(22)-C(9)-C(11)	106	H(31)-C(16)	0.91	H(31)-C(16)-C(15)	112
		H(22)-C(9)-C(13)	110			H(31)-C(16)-H(32)	117
		H(22)-C(9)-C(17)	106				
H(23)-C(8)	0.95	H(23)-C(8)-C(7)	124	H(32)-C(16)	1.08	H(32)-C(16)-C(15)	110
		H(23)-C(8)-C(13)	115				
H(24)-C(7)	0.95	H(24)-C(7)-C(6)	121	H(33)-C(17)	0.97	H(33)-C(17)-C(9)	108
		H(24)-C(7)-C(8)	119			H(33)-C(17)-H(34)	107
						H(33)-C(17)-H(35)	108
H(25)-C(6)	0.96	H(25)-C(6)-C(5)	115	H(34)-C(17)	1.07	H(34)-C(17)-C(9)	106
		H(25)-C(6)-C(7)	124			H(34)-C(17)-H(35)	119
H(26)-C(5)	0.98	H(26)-C(5)-C(6)	125	H(35)-C(17)	0.90	H(35)-C(17)-C(9)	108
		H(26)-C(5)-C(14)	114				

given in Table 2. The coordinates and isotropic temperature factors for the hydrogen atoms and their standard deviations are given in Table 3. The shifts calculated for the parameters in the final cycle of least-squares were all less than one-eighth of the standard deviations.

Description of the structure

A composite of a difference synthesis, for which the contributions of the hydrogen atoms were omitted from F_c , is shown in Fig. 1. No other significant features appeared in the difference map. A stereoscopic view of the molecule is shown in Fig. 2. [Figs. 2, 3 and 4 were drawn on a CALCOMP plotter controlled by an IBM 360/75 computer using the *ORTEP* program (Johnson, 1965).]

The bond distances and angles involving the carbon atoms are shown in Fig. 3. Distances and angles involving hydrogen atoms are listed in Table 4. The standard deviations in the atomic coordinates (Tables 2 and 3) correspond to positional uncertainties of approximately 0.004 Å for the carbon atoms and 0.03 Å for the hydrogen atoms. The standard deviations are thus expected to be about 0.005 Å for C–C distances, 0.03 Å for C–H distances, about 20' for C–C–C angles, about 2° for C–C–H angles and about 3° for H–C–H angles. A comparison of chemically equivalent bond lengths and angles suggests that the standard deviations of the atoms are reasonable.

An attempt to interpret the anisotropic temperature parameters of the carbon atoms in terms of rigid-body motion (Schomaker & Trueblood, 1968) proved to be unsuccessful. The root-mean-square deviations between the observed values of U_{ij} and those calculated on the assumption of rigid-body motion for various groupings are as follows:

Atoms included in the analysis	r.m.s. $\Delta U_{ij}(\text{Å}^2)$
C(1)–C(17)	0.0033
C(1)–C(14)	0.0032
C(1)–C(4), C(9)–C(12)	0.0029
C(5)–C(10), C(13) and C(14)	0.0028.

Since the average estimated standard deviation of the parameters U_{ij} for the various atoms is about 0.0021 Å², it must be concluded that none of the above groupings can be adequately represented as a rigid body.

The equations of the least-squares plane through the benzene rings and the deviations of the individual atoms from their respective planes are given in Table 5.

Table 5. *Least-squares planes of the benzene rings and atomic deviations from the plane*

Coefficients are direction cosines relative to the crystallographic axes. Atoms C(9) and C(10) were not included in the calculations of the least-squares planes.

Plane through C(1), C(2), C(3), C(4), C(11) and C(12)

$$-0.7030X + 0.3256Y + 0.6322Z = 0.570$$

	Deviation
C(1)	0.0085 Å
C(2)	-0.0013
C(3)	-0.0079
C(4)	0.0096
C(11)	-0.0067
C(12)	-0.0022
C(9)	0.0126
C(10)	-0.0411

Plane through C(5), C(6), C(7), C(8), C(13) and C(14)

$$0.6547X + 0.1423Y - 0.7424Z = 3.406$$

	Deviation
C(5)	-0.0014 Å
C(6)	0.0020
C(7)	-0.0021
C(8)	0.0018
C(13)	-0.0013
C(14)	0.0011
C(9)	0.0047
C(10)	0.0458

A stereoscopic view down the c axis showing the packing of the molecules in the unit cell is given in Fig. 4. There are no short contacts between the molecules. The shortest carbon-to-hydrogen intermolecular distance is 2.90 Å between H(20) of the base molecule and C(16) of the molecule in equivalent position $x - \frac{1}{2}, 1 - y, z$. The shortest hydrogen-to-hydrogen intermolecular distance is 2.42 Å between H(32) of the base molecule and H(19) of the molecule in the equivalent position $1 - x, 1 - y, z - \frac{1}{2}$.

The authors gratefully acknowledge the preparation of drawings by Miss Lillian Casler.

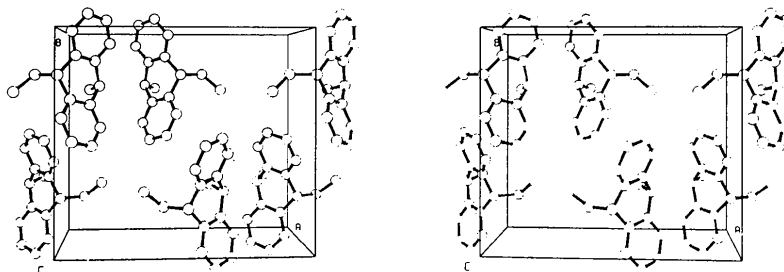


Fig. 4. A stereoscopic view down the c axis showing the packing of the molecules in the unit cell.

This work was supported in part by Grant 6617X from the National Science Foundation and Grant 12121 from the United States Public Health Service.

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Acta Cryst. (1973). **B29**, 318

The Crystal Structure of Ammonium Hydrogen Oxalate Hemihydrate

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(Received 7 September 1972; accepted 23 October 1972)

Crystals of $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ are orthorhombic (space group *Pnma*) with $a = 11.228$, $b = 12.329$, $c = 6.898$ Å; $\rho = 1.614$ g cm⁻³; $Z = 8$. The crystal structure was determined by direct methods. Full-matrix least-squares refinement with anisotropic temperature parameters for non-hydrogen atoms converged to an *R* index of 0.030. The C_2O_4 group is found to be planar, the C–C distance being 1.548 Å. The crystal structure consists of infinite chains of hydrogen oxalate ions linked by hydrogen bonds (2.561 Å). These chains are connected transversely by weaker hydrogen bonds (2.780 Å) and by ionic bonds. Coordination and rotational stability of the NH_4^+ ions are discussed. The relationship of the crystal structure to various physical properties is considered.

Introduction

Single crystals of ammonium hydrogen oxalate hemihydrate exhibit an extremely large elastic anisotropy (Küppers, 1972*b*). This behaviour could possibly be explained in terms of special characteristics associated with interatomic bonds. Therefore, a structure analysis of $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ seemed desirable.

Structures of several oxalates have been previously investigated. In general these investigations reveal planar or nearly planar configurations of oxalate ions and an abnormally long C–C distance. It is a further purpose of this paper to present additional information concerning configurations of oxalate groups.

Experimental

$\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is orthorhombic. Large single crystals were prepared by evaporation from aqueous solution (Küppers, 1972*a*). The density of well-developed specimens (all dimensions approximately one cm) was measured by flotation and was found to be $\rho = 1.613$ g cm⁻³ at 20°C. Unit-cell parameters (designated ac-

cording to Groth, 1910) determined with a single-crystal diffractometer were: $a = 11.228 \pm 0.003$, $b = 12.329 \pm 0.003$, $c = 6.898 \pm 0.002$ Å. Silicon ($a = 5.43064$ Å) was used as a calibrating substance. From these measurements, and assuming $Z = 8$, a water content of $\frac{1}{2}\text{H}_2\text{O}$ per formula unit is obtained. This is in contrast to data given by Groth (1910), who quotes the formula as $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The density calculated from X-ray measurements is $\rho = 1.614$ g cm⁻³. This determination also shows that in the axial ratios cited by Groth (1910), 0.4524:1:0.5592, the first ratio should be doubled.

No measurable piezoelectric effect was observed. This result in addition to systematic absences indicated that the space group is *Pnma*. X-ray intensities were measured with a Siemens automatic diffractometer using Mo $K\alpha$ radiation. The specimen for structure analysis was a crystal with a prismatic habit along [001]. Diameter and length were about 0.7 mm. 1392 independent intensities up to a maximum Bragg angle of $2\theta = 58^\circ$ were determined. Each of these values is an average of four measurements of equivalent reflexions.

No absorption correction was considered necessary because the specimen had relatively equal dimensions and also because the linear absorption coefficient is only 1.7 cm⁻¹ for this compound.

* This investigation was performed in collaboration with the Institut für Kristallographie of the Technische Hochschule Aachen.