

Anisotropic refinement of the crystal structure converged at $R(\text{unweighted}) = 0.066$ and $R(\text{weighted}) = 0.043$.* A list of positional and thermal parameters with estimated standard deviations is given in Table 1. Atomic distances and valence angles are shown in Tables 2 and 3.

Discussion. The structure given by Seemann (1955) with $R = 26\%$ has been confirmed and distinctly improved. $[\text{SiO}_4]$ tetrahedra are corner linked to *Zweierketten* parallel to $[001]$. As in other silicates the Si—O bonds to the bridging oxygen, O(2), are remarkably longer than those to the terminal oxygens, O(1), in accordance with the d_π - p_π bond theory of Cruickshank (1961). The value $124.1(7)^\circ$ for the Si—O—Si valence angle is rather low compared with the mean value, 137° , reported by Cameron, Sueno, Prewitt & Papike (1973) for pyroxenes.

McDonald & Cruickshank (1967) and Seemann (1955) respectively pointed out that in the isostructural $(\text{Na}_2\text{SiO}_3)_x$ the sodium ion occupies the approximate centre of a trigonal bipyramid while in $(\text{Li}_2\text{SiO}_3)_x$ the lithium ion has moved to one corner of the bipyramid, giving a $[4+1]$ coordination with 2.02, 2.05, 2.11, 2.14 and 2.58 Å as Li—O distances. The values given in Table 3 reveal that the Li ions have moved even further into one half of the bipyramid, resulting in a normal tetrahedral $[\text{LiO}_4]$ coordination. $(\text{Li}_2\text{SiO}_3)_x$ may be regarded as a framework of corner-linked $[\text{LiO}_4]$ and $[\text{SiO}_4]$ tetrahedra which is demonstrated by Fig. 1. As McDonald & Cruickshank (1967) have pointed out,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32268 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

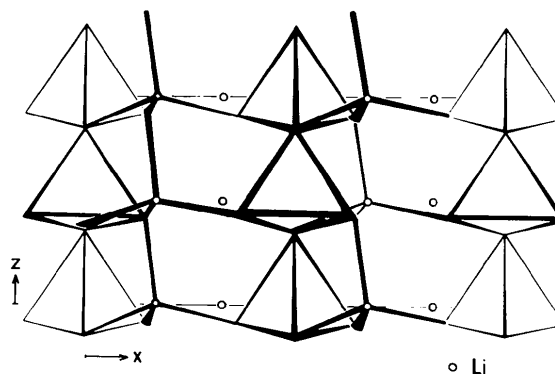


Fig. 1. Projection of $(\text{Li}_2\text{SiO}_3)_x$ along $[010]$.

the topology of this framework is identical with that of wurtzite, the hexagonal polymorph of ZnS.

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7-Chloromethylbenz[*a*]anthracene*

BY DAVID E. ZACHARIAS

The Institute for Cancer Research, The Fox Chase Cancer Center, Philadelphia, PA 19111, USA

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Abstract. $\text{C}_{19}\text{H}_{13}\text{Cl}$, monoclinic, $P2_1/n$, $a = 14.381(7)$, $b = 4.228(2)$, $c = 22.141(7)$ Å, $\beta = 95.87^\circ(5)$, $V = 1339(2)$ Å³, $Z = 4$, $D_x = 1.370$, $D_m = 1.367$ g cm⁻³

(by flotation in 1,1-dichloroethane–1,2-dibromoethane mixture), $F.W. = 276.77$, $\lambda(\text{Cu } K) = 1.5418$ Å, $\mu(\text{Cu } K) = 23.2$ cm⁻¹. The structure was solved by the direct phasing method and refined from 1717 diffractometer data $[I_o \geq 2.33\sigma(I)]$ to $R = 0.063$, $wR = 0.064$. The ring system is essentially planar with the maximum atomic deviation ± 0.05 Å. The Cl atom

* Preliminary details of this structure were presented at the Tenth International Congress, IUCr, Amsterdam, The Netherlands, August 1975.

lies 1.47 Å above and its attached C atom 0.16 Å below this plane.

Introduction. Benz[a]anthracene is a known carcinogen. The title compound is a simple derivative of this substance, having alkylating capability through the chloromethyl group, and is likewise carcinogenic (Peck, Tan & Peck, 1976). The mechanism of chemical carcinogenesis is under intensive investigation. So far, indications are that carcinogenesis results from a combination of the chemical reactivities and geometric configurations of both the causative and the target molecules. This study was undertaken to obtain details of the molecular geometry for comparison with those of other compounds of similar biological activity (Glusker, Zacharias & Carrell, 1976). Crystals were provided by Dr R. M. Peck of this Institute.

Prismatic yellow crystals, elongated along *b*, were grown from benzene-petroleum spirit and exhibited the systematic absences $h00$, $0k0$, $00l$ (h, k, l odd), $h0l$ ($h + l$ odd). A Syntex P1 diffractometer was used to collect data on a crystal, $0.15 \times 0.3 \times 0.4$ mm in size, with

variable $\theta-2\theta$ scans in the 2θ range $0-140^\circ$ and monochromatized Cu $K\alpha$ radiation. Of the approximately 3070 unique reflections theoretically accessible, 2490 (81.3%) were measured and of these, 773 were below the threshold criterion $I_o \geq 2.33\sigma(I_o)$ where $\sigma(I_o)$ is derived from counting statistics. The data, which showed no loss of intensity during collection, were converted to structure amplitudes with Lorentz and polarization corrections and placed on an absolute scale with a Wilson (1942) plot. No absorption correction was made.

The structure was determined from phases obtained from the *SINGEN* and *PHASE* programs of the X-RAY system (Stewart, 1972). Full-matrix least-squares anisotropic refinement (Carrell, 1975) of non-hydrogen atoms was followed by a difference Fourier synthesis in which all H atoms were located. Further anisotropic refinement (H atoms isotropic) gave the final residuals, $R = 0.063$, $wR = 0.064$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$ for reflections above the threshold. In this equation, $\sigma(F) = (F/2)\{\sigma^2(I)/I^2 + \delta^2\}^{1/2}$, where δ is the measured

Table 1. Final atomic parameters

Positional parameters are given as fractions of cell edges. Anisotropic temperature factors are expressed as:

$$\exp[-\frac{1}{4}(h^2a^*{}^2B_{11} + k^2b^*{}^2B_{22} + l^2c^*{}^2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})],$$

and isotropic temperature factors as $\exp(-B \sin^2 \theta/\lambda^2)$ with B values given in Å². The standard deviations for each parameter, determined from the inverted full matrix, are given in parentheses and apply to the last specified digits. Positional parameters for hydrogen atoms are $\times 10^3$, for other atoms $\times 10^4$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cl	-1052 (1)	2704 (3)	4366 (1)	8.01 (4)	4.55 (4)	7.80 (3)	-0.15 (9)	4.51 (8)	-0.60 (10)
C(1)	171 (3)	-1266 (9)	1388 (2)	6.70 (18)	4.74 (19)	5.43 (17)	-0.51 (34)	1.26 (31)	-0.30 (32)
C(2)	-259 (3)	-1557 (10)	806 (2)	9.26 (24)	5.48 (23)	5.47 (19)	-1.14 (41)	0.83 (39)	-0.73 (37)
C(3)	-1136 (3)	-233 (12)	654 (2)	8.77 (26)	6.12 (25)	6.50 (23)	-1.82 (49)	-1.02 (44)	0.13 (42)
C(4)	-1561 (3)	1357 (11)	1083 (2)	6.86 (21)	5.74 (23)	7.30 (25)	-1.19 (41)	-0.21 (40)	1.06 (42)
C(5)	-1578 (2)	3445 (9)	2127 (2)	5.02 (17)	4.76 (21)	7.70 (21)	-0.06 (31)	1.30 (34)	0.89 (36)
C(6)	-1184 (3)	3810 (10)	2695 (2)	5.84 (18)	4.08 (18)	6.95 (21)	0.09 (31)	2.17 (36)	0.34 (36)
C(7)	155 (2)	2965 (8)	3481 (1)	5.63 (14)	2.56 (15)	5.32 (15)	-0.36 (26)	2.27 (27)	-0.16 (27)
C(8)	1495 (3)	1749 (9)	4270 (2)	7.10 (18)	3.99 (19)	5.08 (15)	-0.80 (32)	1.93 (30)	-0.34 (30)
C(9)	2336 (3)	392 (11)	4421 (2)	6.76 (20)	5.77 (23)	5.41 (19)	-1.35 (41)	0.49 (35)	0.29 (37)
C(10)	2800 (3)	-1201 (10)	3990 (2)	5.70 (18)	5.42 (22)	6.23 (21)	-0.34 (37)	0.82 (34)	0.80 (37)
C(11)	2399 (2)	-1484 (9)	3417 (2)	5.48 (17)	4.64 (20)	5.72 (19)	0.02 (30)	1.79 (32)	0.33 (32)
C(12)	1068 (2)	-497 (9)	2646 (2)	5.31 (15)	3.44 (16)	5.12 (15)	-0.18 (28)	2.31 (28)	-0.15 (29)
C(13)	199 (2)	781 (8)	2455 (2)	4.79 (14)	3.25 (16)	4.93 (15)	-0.61 (29)	1.68 (27)	0.19 (28)
C(14)	-240 (2)	377 (9)	1838 (2)	5.48 (16)	3.76 (17)	5.12 (17)	-0.95 (30)	1.37 (31)	0.33 (30)
C(15)	-1136 (3)	1736 (9)	1676 (2)	5.62 (18)	4.22 (20)	6.00 (21)	-0.96 (34)	0.78 (36)	0.77 (35)
C(16)	-268 (2)	2533 (9)	2893 (2)	4.85 (14)	2.94 (14)	5.47 (17)	-0.30 (31)	1.89 (28)	0.41 (33)
C(17)	-298 (3)	4988 (10)	3925 (2)	6.64 (18)	3.76 (17)	6.34 (19)	-0.33 (33)	2.66 (34)	-0.55 (33)
C(18)	1038 (3)	1586 (8)	3668 (2)	5.58 (16)	2.96 (16)	4.75 (17)	-0.89 (27)	1.79 (31)	-0.01 (27)
C(19)	1500 (2)	-138 (9)	3233 (2)	5.06 (15)	3.40 (15)	4.40 (17)	-0.42 (30)	1.68 (30)	0.16 (29)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	76 (3)	-226 (10)	149 (2)	7.6 (12)	H(9)	263 (3)	47 (10)	481 (2)	7.0 (12)
H(2)	7 (3)	-253 (12)	48 (2)	10.2 (13)	H(10)	340 (3)	-220 (12)	412 (2)	7.6 (14)
H(3)	-144 (3)	-25 (11)	23 (2)	9.0 (12)	H(11)	268 (2)	-240 (9)	308 (2)	7.1 (10)
H(4)	-214 (3)	228 (12)	96 (2)	9.9 (16)	H(12)	139 (2)	-159 (9)	234 (2)	5.9 (9)
H(5)	-217 (3)	423 (11)	200 (2)	8.5 (13)	H(171)	-72 (3)	673 (11)	371 (2)	8.6 (13)
H(6)	-150 (2)	480 (10)	303 (2)	8.0 (11)	H(172)	15 (3)	605 (10)	424 (2)	6.9 (11)
H(8)	121 (2)	263 (10)	458 (2)	7.0 (10)					

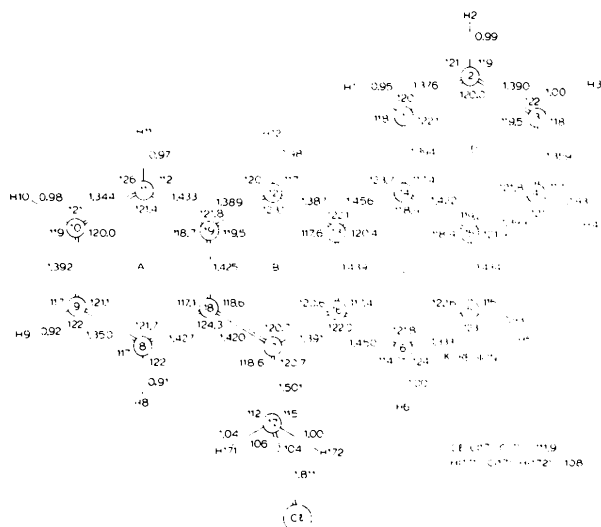


Fig. 1. Bond lengths and interbond angles. Estimated standard deviations for non-hydrogen bond lengths and angles are 0.003–0.005 Å and 0.4°; the average e.s.d.'s for those involving hydrogen are 0.04 Å and 2.5°.

instrumental uncertainty (0.012 for this experiment). Zero weights were assigned to reflections below the threshold. The atomic scattering factors for Cl and C were those in *International Tables for X-ray Crystallography* (1962) and for H those of Stewart, Davidson & Simpson (1965) were used. The final atomic parameter values are given in Table 1* and Fig. 1 gives the corresponding bond lengths and angles.

Discussion. The benz[*a*]anthracene nucleus is essentially planar. The equation of the least-squares best plane through the fused rings, referred to orthogonal axes (Stewart, 1972) is $-0.4679X - 0.8429Y + 0.2655Z = 1.2937$. The angle between the normals to rings *A* and *D* is 1.6°. The bond distances found reflect the variations ascribable to the double-bond positions in the five possible valence-bond representations of the resonance forms of the nucleus. This information is

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summarized in Fig. 2 and Table 2. The angles are within the range of expected values.

The C(17)–Cl bond length, 1.811 Å, is significantly larger than 1.767 Å, the average found for Csp^3 –Cl bonds (Sutton, 1958), and is indicative of the incipient charge separation $R-CH_2^{\delta+}-Cl^{\delta-}$ which accounts for the alkylating ability of this molecule.

In the crystal, the molecules pack stepwise in planes 3.56 Å apart along the *b* direction. Fig. 3 is a view of the stacking normal to the plane through the aromatic rings and shows that there is very little overlap between adjacent aromatic portions.

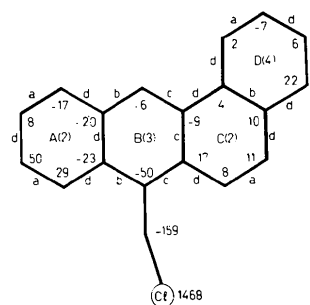


Fig. 2. Summary of least-squares best plane and valence-bond representation information. The number at each atom is the distance ($\text{Å} \times 10^3$) above or below the plane through the aromatic ring system. The number in parentheses in each ring is the number of times that ring is a benzene ring in the valence-bond representations. The letter at each bond represents the percent double-bond character as given in Table 2.

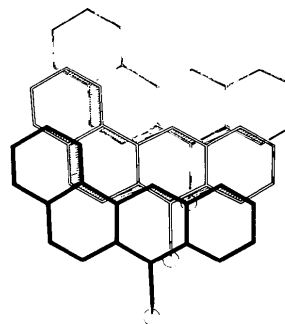


Fig. 3. Stacking of the molecules viewed normal to the least-squares best plane through the aromatic portion.

Table 2. Analysis of valence-bond representations of resonance forms of benz[*a*]anthracene in 7-chloromethylbenz[*a*]anthracene

Number of bonds	Designation	Number of times a double bond	% of time a double bond	Range of length found, Å	Average length, Å	Calculated length, Å (Pauling, 1960)
5	<i>a</i>	4	80	1.333–1.376	1.352	1.355
3	<i>b</i>	3	60	1.389–1.422	1.410	1.380
3	<i>c</i>	2	40	1.387–1.439	1.406	1.410
10	<i>d</i>	1	20	1.390–1.456	1.420	1.450

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N,N-Bis(2-hydroxyethyl)glycine

BY VIVIAN CODY, JOHN HAZEL AND DAVID LANGS

Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, New York 14203, USA

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Abstract. $C_{16}H_{13}O_4N$ (bicine), m.p. 193°C, monoclinic, $P2_1/n$, $a = 9.963$ (2), $b = 11.045$ (3), $c = 7.667$ (1) Å, $\beta = 111.78$ (2)°, $Z = 4$, $M_r = 163.18$, $D_c = 1.38$ g cm⁻³, observed data $R = 4.7\%$. The conformation of the diethanolamine moiety differs significantly from that observed in other *N*-diethanolamine structures. The hydroxyethyl moiety adopts a staggered conformation as opposed to the *trans* conformation observed in *N*-diethanolamine. There are strong hydroxyl hydrogen bonds with the carboxylic O atoms in adjacent molecules.

Introduction. Crystals of bicine were produced as a by-product of crystallization of the thyroid hormone analogue 3,5-diisopropyl-3'-iodo-DL-thyronine with *N*-diethanolamine in methanol. The melting point of the crystals is 195°C with slight decomposition, in agreement with that previously found for bicine (Stecher, 1968). A 0.1 × 0.1 × 0.2 mm crystal was used to measure the lattice parameters and intensities. The data showed the systematic absences for the space group $P2_1/n$ and the cell constants were determined by least-squares analysis of the angular settings of 45 reflections [at 20°C; $\lambda(\text{Mo } K\alpha) = 0.7091$ Å]. The intensities of 2254 reflexions (1134 reflexions had $I > 2\sigma$) with $2\theta < 60^\circ$ were measured on a Nonius CAD-4 automated diffractometer using Mo $K\alpha$ radiation. After the usual Lorentz and polarization corrections had been applied, normalized structure-factor amplitudes were computed and the structure was solved by application of direct

methods with *MULTAN* (Germain, Main & Woolfson, 1971) and *NQUEST* (DeTitta, Edmonds, Langs & Hauptman, 1975).

Initially the composition of the crystal was unknown. *MULTAN*, based on 280 reflexions with $E > 1.60$, computed phases for 64 ambiguities which had 16 combined FOM indicators of 2.98. *NQUEST* was run on the 64 phase sets from *MULTAN* with the following criteria: $E_{\min} = 1.60$, $B_{\min} = 0.30$, E_{\max} (cross-terms) = 5.00 and E_{\min} (cross-terms) = 0.50. This resulted in three values of the *NQUEST* indicator of -0.40 from which *E* maps were computed. The next best *NQUEST* indicator was -0.17. An *E* map calculated from a *MULTAN* solution with an *NQUEST* value of -0.40 produced a linear fragment of reasonable geometry. Subsequent Fourier maps produced a molecule that was recognized as bicine.

The atomic parameters were refined by full-matrix least-squares calculations. After three cycles of anisotropic refinement, a difference Fourier map was computed which produced positions for all 13 H atoms. The parameters of all atoms including the H atoms were refined for three final cycles. The weights used were the quantities $(1/\sigma_F^2)$ where σ_F is defined by Stout & Jensen (1968, equation H.14) and the instability correction was 0.06 rather than 0.01. The *R* index, defined as $\Sigma |F_o| - |F_c| / \Sigma |F_o| \times 100$, was 8.2% for all data and 4.7% for the 1134 reflections used in the refinement. The Fourier and least-squares programs are part of the Nonius crystallographic package for the PDP 11/45.