References

Bats, J. W. (1977). *Acta Cryst.* B**33**, 466–472.

Bats, J. W. & Coppens, P. (1975). *Acta Cryst.* B**31**, 1467–1472.

Bats, J. W., Coppens, P. & Koetzle, T. F. (1977). *Acta Cryst.* B**33**, 37–45. Corrigendum: B**33**, 1304.

Bats, J. W., Coppens, P. & Kvick, Å. (1977). *Acta Cryst.* B**33**, 1534–1542.

Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.

Chipman, D. R. (1969). *Acta Cryst.* A**25**, 209–213.

Coppens, P. (1975). *Phys. Rev. Lett.* **35**, 98–100.

Coppens, P., Pautler, D. & Griffin, J. F. (1971). *J. Amer. Chem. Soc.* **93**, 1053–1058.

Coppens, P., Ross, F. K., Blessing, R. H., Cooper, W. F., Larsen, F. K., Leipoldt, J. G., Rees, B. & Leonard, R. (1974). *J. Appl. Cryst.* **7**, 315–319.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Wang, Y., Blessing, R. H., Ross, F. K. & Coppens, P. (1976). *Acta Cryst.* B**32**, 572–578.

Acta Cryst. (1977). B**33**, 2041–2047

The Structure of a Cyclodimer from Reaction of 7-Methoxy-1,2-dihydronaphthalene with Sodium and Ethylenediamine. A Comparison of Bond Distances and Angles in Two Molecules

By Dick van der Helm and Kang Kun Wu

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, USA

and L. L. Ansell, P. H. Ruehle and E. J. Eisenbraun

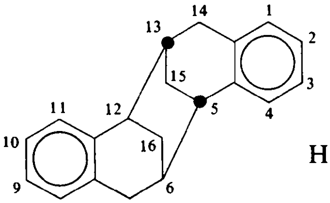
Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074, USA

(*Received* 30 *August* 1976; *accepted* 9 *December* 1976)

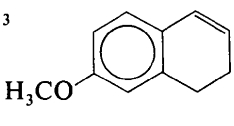
6,6a,7,12,13,13a-Hexahydro-2,9-dimethoxy-7,13-methano-5*H*-benzo[4,5]cyclohepta[1,2-*a*]naphthalene, $C_{22}H_{24}O_2$, is a cyclodimerized product obtained from reaction of 7-methoxy-1,2-dihydronaphthalene with sodium and ethylenediamine. The preparation, isolation, and spectral data of this dimer are described. Crystals of the compound are monoclinic, space group $P2_1/c$. The cell dimensions are $a = 26\cdot643\,(9)$, $b = 8\cdot165\,(3)$, $c = 16\cdot226\,(5)$ Å and $\beta = 107\cdot56\,(2)°$. The structure was determined by direct methods and refined with least-squares calculations on 6372 data collected at −160°C. The final R value is 0·060. The asymmetric unit contains two independent molecules which show good agreement of distances for corresponding bonds. It is concluded that the standard deviations calculated from the inverse of the least-squares matrix are not underestimated.

Introduction

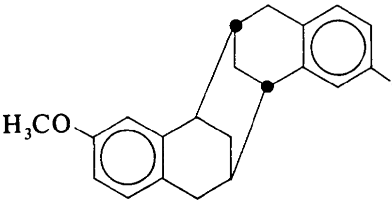
The synthesis and crystallographic structure of 5,6,7,12,13,14-hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecane (I) were recently reported (Eisenbraun, Ansell, Dobbs, Harris, Hertzler, Ruehle, Burks & van der Helm, 1976) as a product obtained from reaction of naphthalene with sodium in ethylenediamine. Obtaining this unusual structure prompted extension of the reaction to 7-methoxy-1,2-dihydronaphthalene (II) in an effort to learn whether methoxylated dimers comparable to hydrocarbon I could be obtained. Dimers III, IV, and V are isolated as reaction products from treatment of II with sodium and ethylenediamine (Ansell, 1976). The mass spectral data of title compound V shows an *m/e* of 320, which strongly suggests a cyclodimer or an unsaturated monolinked dimer. The latter structural possibility is excluded by absence of vinyl proton signals in the ^{1}H NMR spectrum. Furthermore, the complexity of the ^{1}H NMR spectrum indicates lack of symmetry and a skeletal difference from symmetric dimers I and III which have simpler spectra. The complexity of the analytical data as well as the limited amount of material available for chemical degradation prompted X-ray crystallographic analysis of dimer V. The hydrocarbon skeleton, stereochemistry, and positions of methoxyl groups of racemic 6,6a,7,12,13,13a-hexahydro-2,9-dimethoxy-7,13-methano-5*H*-benzo[4,5]cyclohepta[1,2-*a*]naphthalene (V) are now assigned by X-ray crystallographic analysis.



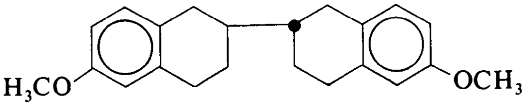
I



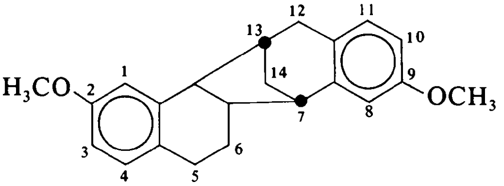
II



III



IV



V (one enantiomer)

Experimental

Synthesis

A sample of II (50 g, 0·31 mol) was stirred with sodium (20 g) and ethylenediamine (700 ml) at 45 °C for 3 h with a stir-shredding device similar to that described for the preparation of hydrocarbon I (Eisenbraun *et al.*, 1976). A similar isolation procedure was used to obtain a crude oil which was distilled (Kugelrohr) to give a fraction boiling at 120°C (0·05 mm) containing mostly 6-methoxytetralin (2·3 g, 4·5%). Further heating to 230 °C (0·05 mm) gave a fraction containing dimers (24·2 g, 49%). A pot residue (16·0 g, 32%) remained.

The distilled dimer mixture from the previous procedure was dissolved in ether and was cooled to −14 °C for 24 h. The first crop of crystals contained only dimer IV. Subsequent crops, obtained by alternately concentrating and cooling the mother liquor, contained mixtures of III and IV. This procedure was repeated until crystals no longer formed. The mother liquor was pumped to remove solvent and then stored at −14 °C. Large crystals of V slowly formed during several days. These crystals were washed with isohexane to remove adhering oil.

Crude V (4·0 g), isolated from the oil, was recrystallized from ethanol (100 ml) to give 3·0 g of colorless V, m.p. 110–112 °C; mass spectrum (70 eV) m/e (relative intensity) 320 (M^+, 100), 161 (27), 160 (78), 159 (70), 144 (19), and 115 (32); IR spectrum (KBr) 8·0 μm (C—O—C asymmetric stretch), 9·6 μm (C—O—C symmetric stretch); NMR spectrum ($CDCl_3$) δ 7·06–6·82 (*m*,3,ArH), 6·67–6·54 (*m*,3,ArH), 3·76 (*s*,6,$ArOCH_3$), 3·18–2·12 (envelope,8,$ArCH_2$ and $ArCH_2CH$), 2·10–1·74 (*m*,2,$ArCH_2CH_2$), 1·68–1·22 (*m*,2,$ArCH_2CH_2$); UV spectrum max. (95% ethanol) 279 nm (log ε 3·71), 287 (3·67). Analysis calculated for $C_{22}H_{24}O_2$: C, 82·46; H, 7·55; found: C, 82·64; H, 7·64.

Crystallographic data

Crystals of the title compound were grown from 50% EtOH/50% acetone solution. Preliminary investigation of the crystals by rotation and Weissenberg photographs showed that most of the crystals are twinned. A single crystal with the dimension of 0·17 × 0·25 × 0·29 mm was found. The space group was determined to be monoclinic, $P2_1/c$. The least-squares cell dimensions with Cu $K\alpha_1$ (λ = 1·5405 Å) at liquid nitrogen temperature (−160 °C) were determined from the 2θ values of 44 reflections distributed through all octants of reciprocal space. The crystal data are $C_{22}H_{24}O_2$; FW 320·4, space group $P2_1/c$; a = 26·643 (9), b = 8·165 (3), c = 16·226 (5) Å, β = 107·56 (2)°; Z = 8; V = 3365·3 Å^3; $F(000)$ = 1376; D_c = 1·265 (at −160 °C), D_c = 1·234 (at 26 °C), D_m = 1·229 g cm^{-3} (measured at room temperature by flotation method in KI aqueous solution).

The intensities of 6372 reflections with $2\theta \leq 140$ were measured at liquid nitrogen temperature (−160°C) with Ni-filtered Cu $K\alpha$ radiation (λ = 1·5418 Å) on a Nonius CAD-4 automatic diffractometer. The data were collected with θ–2θ scans in which the θ-scan width was calculated as (0·8 + 0·08 tan θ)°. The maximum scan time was 50 s with $\frac{2}{3}$ of the time used for scanning the peak and $\frac{1}{3}$ used for scanning both high-θ and low-θ backgrounds. For 672 reflections, the intensities were less than twice the standard error based on counting statistics and were assigned intensities of $1 \cdot 4T^{1/2}$ (T is the total count) for the purposes of least-squares refinement. Experimental weights were assigned to each reflection (Ealick, van der Helm & Weinheimer, 1975). Lorentz and polarization corrections were applied. Absorption corrections were not calculated (μ = 6·3 cm^{-1}).

Table 1. *Positional parameters and isotropic thermal parameters for carbon and oxygen atoms*

An asterisk indicates values converted from anisotropic thermal parameters. Standard deviation for isotropic temperature factors is 0·03 Å² for C and O atoms. Standard deviation for last digit is in parentheses.

	Molecule *A*				Molecule *B*			
	$x \times 10^5$	$y \times 10^4$	$z \times 10^4$	B(Å²)	$x \times 10^5$	$y \times 10^4$	$z \times 10^4$	B(Å²)
C(1)	97331 (7)	8392 (2)	3778 (1)	1·58	47181 (7)	6708 (2)	5959 (1)	1·58
C(2)	92982 (7)	8991 (2)	3130 (1)	1·66	42695 (7)	6140 (2)	6145 (1)	1·64
C(3)	93249 (7)	10511 (2)	2758 (1)	1·85	42684 (8)	4596 (2)	6502 (1)	1·87
C(4)	97890 (8)	11412 (2)	3045 (1)	1·88	47227 (8)	3647 (3)	6686 (1)	1·92
C(4a)	102237 (7)	10838 (2)	3703 (1)	1·60	51725 (7)	4192 (2)	6501 (1)	1·96
C(5)	107176 (8)	11850 (2)	4019 (1)	1·75*	56581 (8)	3136 (2)	6700 (1)	1·87*
C(6)	111997 (7)	10746 (3)	4290 (1)	1·74*	61480 (8)	4201 (3)	6955 (1)	1·96*
C(6a)	111713 (7)	9604 (2)	5027 (1)	1·54	61525 (7)	5332 (2)	6208 (1)	1·60
C(7)	115961 (7)	8242 (2)	5208 (1)	1·63	65936 (7)	6642 (2)	6482 (1)	1·71
C(7a)	116977 (7)	7542 (2)	6108 (1)	1·52	67261 (7)	7284 (2)	5697 (1)	1·55
C(8)	121496 (7)	7953 (2)	6770 (1)	1·62	71643 (7)	6707 (2)	5492 (1)	1·64
C(9)	122433 (7)	7302 (2)	7598 (1)	1·67	72776 (7)	7246 (2)	4751 (1)	1·60
C(10)	118775 (7)	6258 (2)	7776 (1)	1·68	69500 (7)	8381 (2)	4210 (1)	1·74
C(11)	114253 (7)	5851 (2)	7111 (1)	1·67	65094 (7)	8954 (2)	4418 (1)	1·69
C(11a)	113307 (7)	6458 (2)	6278 (1)	1·57	63896 (7)	8425 (2)	5151 (1)	1·60
C(12)	108558 (7)	5877 (2)	5558 (1)	1·73	59131 (7)	9096 (2)	5367 (1)	1·85
C(13)	107890 (7)	6816 (2)	4712 (1)	1·73	58053 (7)	8172 (2)	6121 (1)	1·74
C(13a)	106420 (7)	8637 (2)	4819 (1)	1·46	56371 (7)	6365 (2)	5859 (1)	1·48
C(13b)	101962 (7)	9298 (2)	4069 (1)	1·47	51704 (7)	5748 (2)	6131 (1)	1·52
C(14)	113266 (8)	6927 (3)	4548 (1)	1·80*	63241 (8)	7999 (3)	6848 (1)	1·94*
O(15)	88638 (5)	7989 (2)	2909 (1)	2·05*	38471 (5)	7193 (2)	5946 (1)	1·76*
C(16)	84086 (8)	8552 (3)	2256 (1)	2·02*	33902 (7)	6672 (3)	6157 (1)	1·79*
O(17)	127018 (5)	7793 (2)	8197 (1)	2·15*	77142 (5)	6562 (2)	4608 (1)	1·83*
C(18)	128263 (8)	7065 (3)	9033 (1)	2·43*	78205 (9)	6996 (3)	3826 (1)	2·08*

Table 2. *Positional and thermal parameters of hydrogen atoms*

The standard deviations for the thermal parameters are between 0·4 and 0·6 Å².

	Molecule *A*				Molecule *B*			
	$x \times 10^4$	$y \times 10^3$	$z \times 10^3$	B (Å²)	$x \times 10^4$	$y \times 10^3$	$z \times 10^3$	B (Å²)
H(1)	9679 (8)	723 (3)	403 (1)	2·0	4712 (8)	783 (3)	569 (1)	2·2
H(3)	9001 (8)	1094 (3)	228 (1)	1·8	3931 (8)	416 (3)	660 (1)	2·0
H(4)	9810 (9)	1253 (3)	274 (1)	2·5	4727 (9)	245 (3)	697 (2)	2·6
H(5)(1)	10710 (9)	1260 (3)	456 (2)	2·6	5641 (9)	240 (3)	716 (2)	3·1
H(5)(2)	10740 (8)	1267 (3)	357 (1)	1·7	5660 (9)	252 (3)	616 (2)	2·8
H(6)(1)	11205 (8)	1007 (3)	377 (1)	2·2	6490 (9)	349 (3)	712 (2)	2·5
H(6)(2)	11530 (9)	1142 (3)	448 (2)	2·8	6143 (8)	488 (3)	748 (1)	2·2
H(6a)	11222 (8)	1031 (3)	555 (1)	2·0	6194 (8)	463 (3)	572 (1)	1·4
H(7)	11953 (8)	863 (3)	515 (1)	2·0	6920 (8)	616 (3)	689 (1)	2·1
H(8)	12414 (10)	874 (3)	671 (2)	3·3	7378 (8)	589 (3)	586 (1)	1·8
H(10)	11954 (8)	583 (3)	839 (1)	1·9	7020 (8)	873 (3)	366 (1)	1·8
H(11)	11148 (8)	512 (3)	724 (1)	1·7	6272 (9)	985 (3)	402 (2)	2·8
H(12)(1)	10549 (8)	598 (3)	571 (1)	1·2	5601 (9)	901 (3)	483 (1)	2·4
H(12)(2)	10913 (9)	465 (3)	545 (1)	2·6	5982 (9)	1028 (3)	556 (1)	2·6
H(13)	10506 (8)	630 (3)	421 (1)	1·3	5488 (9)	873 (3)	630 (2)	2·7
H(13a)	10508 (8)	867 (3)	535 (1)	1·8	5520 (8)	625 (3)	522 (1)	1·8
H(14)(1)	11542 (9)	581 (3)	464 (1)	2·4	6546 (10)	910 (3)	698 (2)	3·3
H(14)(2)	11293 (8)	738 (3)	395 (1)	1·6	6279 (9)	761 (3)	740 (1)	2·4
H(16)(1)	8475 (9)	875 (3)	168 (2)	3·2	3462 (9)	642 (3)	677 (1)	2·3
H(16)(2)	8292 (8)	952 (3)	245 (1)	2·1	3222 (9)	570 (3)	582 (2)	2·9
H(16)(3)	8160 (9)	772 (3)	220 (1)	2·5	3129 (9)	765 (3)	599 (2)	2·6
H(18)(1)	12557 (9)	730 (3)	932 (2)	2·9	7511 (9)	666 (3)	333 (2)	3·0
H(18)(2)	13185 (9)	758 (3)	935 (2)	2·9	8158 (10)	637 (3)	386 (2)	3·3
H(18)(3)	12829 (10)	582 (3)	896 (2)	3·7	7883 (10)	821 (3)	381 (2)	3·2

Structure determination and refinement

The structure was solved by direct methods with the program *MULTAN* (Germain, Main & Woolfson, 1971) and employing the 420 E values larger than 1·86. The structure was refined by block-diagonal least-squares methods (Ahmed, 1966). The quantity minimized was $\Sigma w_F(|kF_o| - |F_c|)^2$. Successive difference Fourier syntheses showed anisotropy for 14 C and O atoms as well as the location of the H atoms. 20 strong reflections showed evidence of extinction. A secondary isotropic extinction correction was applied in the later cycles of refinement $[F_c^2/F_o^2 = \exp(-2gI_o)$, where $2g = 5{\cdot}35 \times 10^{-6}]$. The final cycles of least-squares refinement used anisotropic thermal parameters for 14 C and O atoms and isotropic parameters for all other atoms. The refinement was terminated when all shifts were less than 0·16 σ. The final agreement index for all 6372 reflections, R $(= \Sigma||kF_o| - |F_c||/\Sigma|kF_o|)$, is 0·060. A final difference Fourier synthesis showed electron densities between −0·3 and 0·5 e Å^{-3} in which the negative peaks were on atom locations and the positive peaks were in the middle of chemical bonds. A structure-factor analysis did not show significant variation of $w_F\Delta_F^2$ with $|F_o|$ or $\sin^2 \theta/\lambda$ validating the weighting scheme used. The final parameters for all atoms are given in Tables 1 and 2.* Bond angles are given in Table 3.

Table 3. *Bond angles* (°)

	Molecule *A*	Molecule *B*
C(1)–C(2)–C(3)	119·9 (2)	120·1 (2)
C(2)–C(3)–C(4)	118·9 (2)	119·0 (2)
C(3)–C(4)–C(4a)	121·7 (2)	121·7 (2)
C(4)–C(4a)–C(13b)	119·1 (2)	119·2 (2)
C(4a)–C(13b)–C(1)	119·1 (2)	119·1 (2)
C(13b)–C(1)–C(2)	121·2 (2)	121·0 (2)
C(1)–C(2)–O(15)	115·5 (2)	115·8 (2)
C(3)–C(2)–O(15)	124·5 (2)	124·1 (2)
C(2)–O(15)–C(16)	117·6 (2)	117·0 (2)
C(1)–C(13b)–C(13a)	118·8 (2)	119·2 (2)
C(4)–C(4a)–C(5)	120·9 (2)	120·7 (2)
C(4a)–C(5)–C(6)	110·3 (2)	110·1 (2)
C(5)–C(6)–C(6a)	110·4 (2)	110·0 (2)
C(6)–C(6a)–C(13a)	113·1 (2)	113·4 (2)
C(6a)–C(13a)–C(13b)	115·5 (2)	114·8 (2)
C(13a)–C(13b)–C(4a)	122·2 (2)	121·6 (2)
C(13b)–C(4a)–C(5)	119·9 (2)	120·1 (2)
C(6)–C(6a)–C(7)	112·2 (2)	112·1 (2)
C(13b)–C(13a)–C(13)	114·2 (2)	115·1 (2)
C(6a)–C(7)–C(7a)	111·1 (2)	110·3 (2)
C(13a)–C(13)–C(12)	110·0 (2)	110·7 (2)
C(6a)–C(7)–C(14)	102·1 (1)	101·9 (2)
C(7)–C(14)–C(13)	100·7 (2)	100·8 (2)
C(14)–C(13)–C(13a)	104·0 (2)	104·0 (2)
C(13)–C(13a)–C(6a)	105·4 (1)	105·2 (1)
C(13a)–C(6a)–C(7)	103·8 (1)	103·8 (1)
C(7)–C(7a)–C(11a)	119·6 (2)	119·5 (2)
C(7a)–C(11a)–C(12)	120·9 (2)	120·8 (2)
C(11a)–C(12)–C(13)	112·2 (2)	112·2 (2)
C(12)–C(13)–C(14)	108·8 (2)	108·5 (2)
C(14)–C(7)–C(7a)	108·6 (2)	109·3 (2)
C(7)–C(7a)–C(8)	121·0 (2)	120·6 (2)
C(12)–C(11a)–C(11)	120·2 (2)	120·6 (2)
C(7a)–C(8)–C(9)	120·9 (2)	121·0 (2)
C(8)–C(9)–C(10)	120·0 (2)	119·8 (2)
C(9)–C(10)–C(11)	118·9 (2)	119·0 (2)
C(10)–C(11)–C(11a)	121·9 (2)	122·0 (2)
C(11)–C(11a)–C(7a)	118·8 (2)	118·5 (2)
C(11a)–C(7a)–C(8)	119·4 (2)	119·8 (2)
C(8)–C(9)–O(17)	115·7 (2)	115·6 (2)
C(10)–C(9)–O(17)	124·3 (2)	124·6 (2)
C(9)–O(17)–C(18)	117·0 (2)	117·1 (2)

The scattering factors of C and O were from *International Tables for X-ray Crystallography* (197[illegible] and those of H were taken from Stewart, Davidson & Simpson (1965).

Results and discussion

There are two crystallographically independent molecules in the asymmetric unit. A stereoscopic view (Johnson, 1965) for both molecules is given in Fig. 1. Although both molecules are shown in the same absolute configuration, the fact that the space group is centrosymmetric requires the crystal to be a racemate. The bond lengths, their standard deviations (given in parentheses) and numbering scheme are shown in Fig. 2. Agreement between corresponding bond lengths in these two molecules is excellent. The largest discrepancy is in the C(6)–C(6a) bond, 1·536 (3) Å in molecule *A* and 1·526 (3) Å in molecule *B*. The range of C–H bond lengths is 0·93 to 1·08 Å.

In order to compare equivalent bond distances (28) and bond angles (42) in the two independent molecules a half-normal probability plot (Abrahams & Keve, 1971) was constructed for the differences in both distances and angles (Fig. 3*a*,*b*). One notes that the slope for the differences in bond distances is less than 1·0, indicating that the standard deviations calculated from the inverse of the least-squares matrix are definitely not underestimated and possibly even overestimated. We feel that the use of low-temperature data is at least a contributing factor to the apparent realism of the calculated standard deviations in that the method reduces the thermal motion of all atoms compared with room temperature. The half-normal probability plot for the bond-angle differences (Fig. 3*b*) shows a slope larger than 1·0. The apparent disagreement is believed to be related to the different environments of the two molecules which cause differences in the bond angles but do not appear to affect the bond distances to any large extent.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32381 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The observations made from Fig. 3 are not artifacts caused by the size of the sample or the type of refinement. Another set of half-normal probability plots was constructed after a refinement in which all O and C atoms were given anisotropic thermal parameters and the general features of the plots are the same as those in Fig. 3 in that the plot for the bond-distance differences has a slope smaller than 1·0 and that for the bond angles a slope larger than 1·0. The slopes are 10–20% larger than those in Fig. 3, caused by the fact that the standard deviations decreased more than the differences in distances and angles.

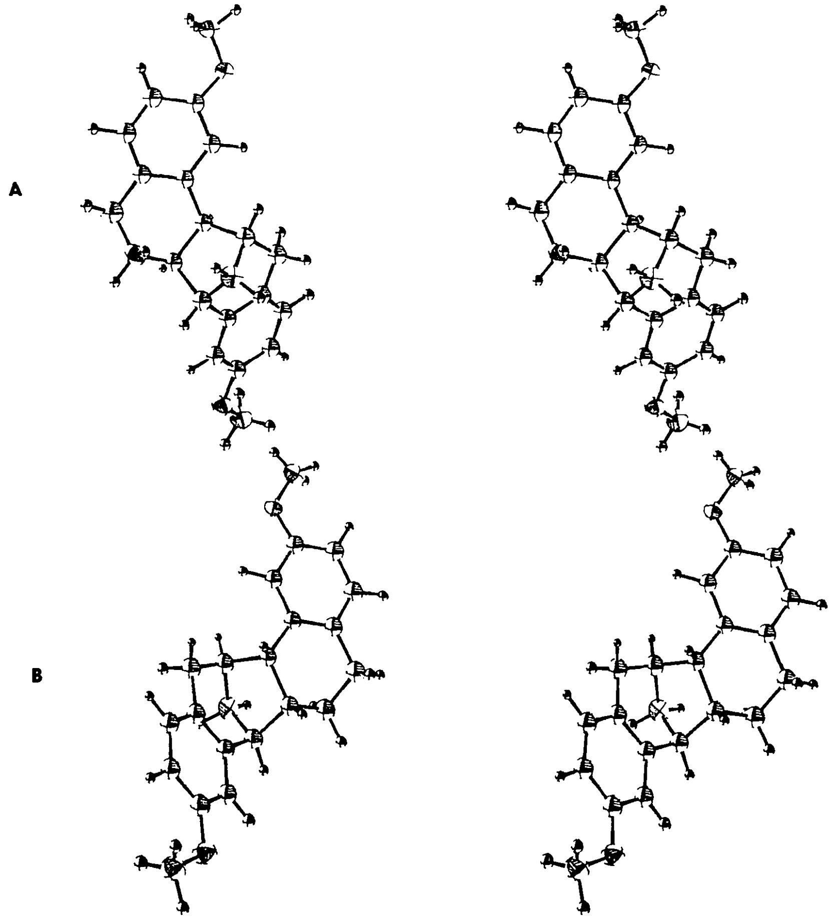


Fig. 1. Stereoview of both independent molecules (Johnson, 1965).

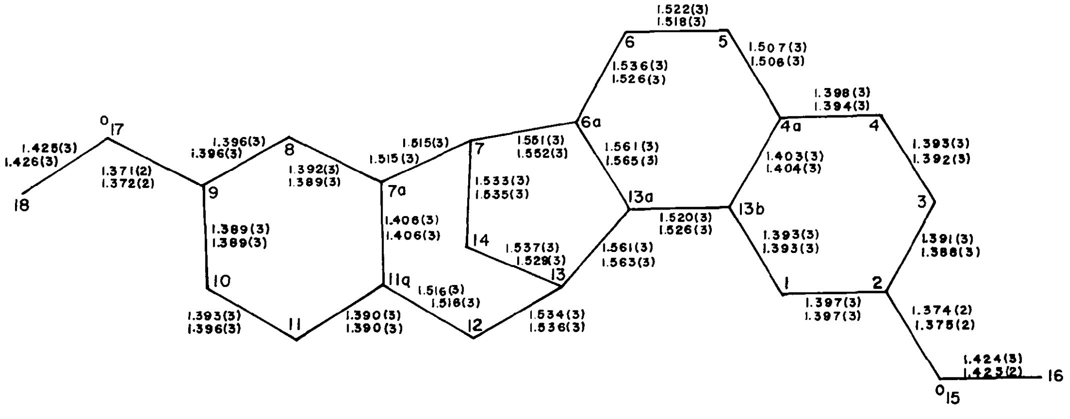
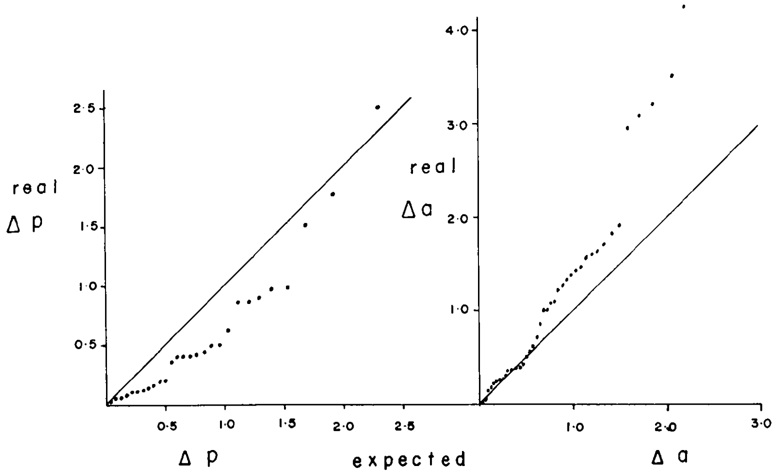


Fig. 2. Bond lengths (Å) and numbering scheme. The lower numbers are for molecule *B*.



(*a*) (*b*)

Fig. 3. Half-normal probability plots comparing the differences in (*a*) bond distances and (*b*) bond angles in the two independent molecules. Expected values are from *International Tables for X-ray Crystallography* (1974).

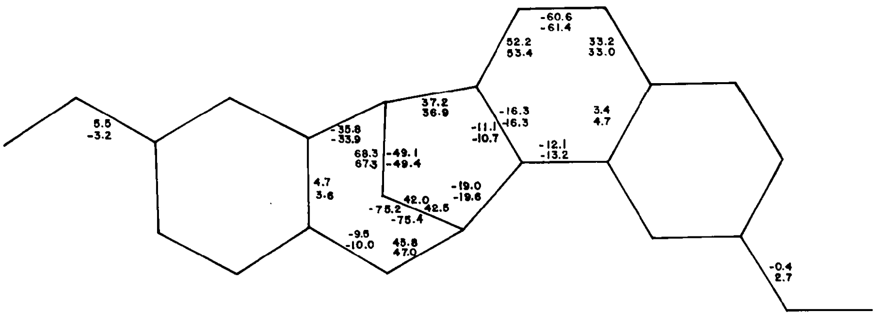


Fig. 4. Conformational angles (°) around the six- and five-membered rings and for the methoxy groups. The lower numbers are for molecule *B*.

We observe in this structure, as well as others for which low-temperature data are used, residual positive electron density in the middle of a number of chemical bonds. This is not caused by anisotropy of the atoms involved, as can be seen from the difference Fourier synthesis, nor is it physically likely, because such peaks, if caused by anisotropy, would indicate a larger than average thermal motion parallel to the chemical bond connecting the atoms, whereas one would expect a smaller than average thermal motion in that direction.

All bond lengths of the methano-bridges are less than 1·54 Å. All bond angles in the five-membered rings are significantly smaller than 108° with the smallest value at C(14). The exo(penta)cyclic angles at C(6a) and C(13a) are larger than expected for a tetrahedral C atom. The methoxy groups are in the plane of the benzene rings to which they are attached (Fig. 4). There is a significant difference in the exocyclic C—C—O angles, which is caused by the intramolecular contacts of the H atoms of the methyl groups and the H atoms bonded to C(3) and C(10) respectively. The endocyclic angles of the benzene rings all show the same pattern in their small deviations from 120°.

There is no previous structure determination of this bridged tetracyclic C skeleton. The closest similarity is found in two photodimers of 6,6′-dimethyl-2,3-benzo-2,4-cycloheptadienone (Biefeld & Barnett, 1974), which show the fused cycloheptene–cyclohexene–benzene ring system. Both these dimers show a similar pattern in the bond angles for the benzene rings and cyclohexene rings, as described for the present structure. No such similarity exists for the cycloheptene ring, which may be expected, being bridged by the methano group in the present structure.

Fig. 4 shows the conformational angles inside the two cyclohexene rings, the five-membered ring, and the methoxy groups. Both cyclohexene rings are in an approximate half-chair form.

There are a few short intramolecular contacts in the carbocyclic system for H atoms separated by two or more C atoms (the values are for molecules *A* and *B* respectively): H(6) (2)—H(14) (2): 2·22, 2·27, H(6a)—H(13a): 2·27, 2·18, H(13)—H(1): 2·26, 2·13 and H(12)(1)—H(13a): 2·27, 2·36 Å. The smallest intermolecular contact is H(15)(1)(*A*)—H(12)(2)(*A*): 2·16 Å.

We wish to thank the Computer Center of the University of Oklahoma for providing the computer facilities. We are grateful to the Contraceptive Development Branch, Center for Population Research, National Institute of Child Health and Human Development (Contract No. N01-HD-2846 to Oklahoma State University) for partial support of this work. We also thank Drs Kurt L. Loening and O. C. Dermer for advice on nomenclature.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

AHMED, F. R. (1966). Program *NRC*-10, National Research Council, Ottawa, Canada.

ANSELL, L. L. (1976). PhD thesis, Oklahoma State Univ.

BIEFELD, C. G. & BARNETT, B. L. (1974). *Acta Cryst.* B**30**, 2411–2421.

EALICK, S. E., VAN DER HELM, D. & WEINHEIMER, A. J. (1975). *Acta Cryst.* B**31**, 1618–1626.

EISENBRAUN, E. J., ANSELL, L. L., DOBBS, T. K., HARRIS, L. E., HERTZLER, D. V., RUEHLE, P. H., BURKS, J. E. JR & VAN DER HELM, D. (1976). *J. Org. Chem.* **41**, 2910–2913.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72, 302. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1977). B**33**, 2047–2051

Model Compounds for Protein Nucleic Acid Interactions. IV. Crystal Structure of a Nucleoside Peptide with Anti-Viral Properties: 5-[*N*-(L-Leucyl)amino]uridine

BY POOJAPPAN NARAYANAN AND HELEN M. BERMAN

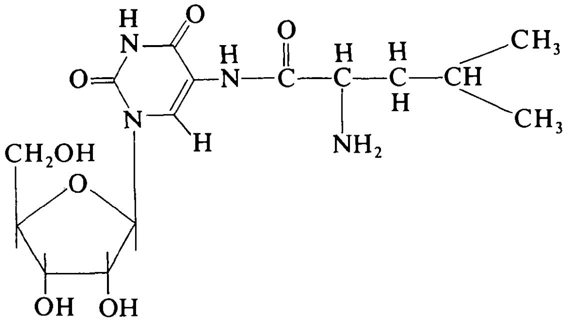
The Institute for Cancer Research, The Fox Chase Cancer Center, Philadelphia, Pennsylvania 19111, *USA*

(*Received* 30 *August* 1976; *accepted* 3 *December* 1976)

The crystal structure of an anti-viral agent, 5-[*N*-(L-leucyl)amino]uridine, has been determined. The compound crystallizes in the orthorhombic system, space group $I222$, with $a = 10{\cdot}883\,(3)$, $b = 23{\cdot}774\,(5)$, $c = 17{\cdot}038\,(7)$ Å, $V = 4408{\cdot}3$ Å^3, $Z = 8$, $d_m = 1{\cdot}34$ g cm^{-3}. The intensities of 1699 independent reflections were collected on an automatic diffractometer with θ–2θ scans and graphite-monochromatized Cu $K\alpha$ radiation. The structure was solved by direct phase determination and refined by full-matrix least squares to an R value of 0·080. The weighted R_w value and goodness of fit are 0·113 and 0·85 respectively. The crystal structure has three distinct regions: a layer of hydrogen-bonded uracil rings, a hydrophobic methyl columnar region and a hydrophilic water channel. There are no hydrogen bonds between the peptide and uracil ring.

Introduction

Nucleoside peptides have been found in nucleic acids (Robins *et al.*, 1971) and often have medicinal properties (Ivanovics, Rousseau & Robins, 1971). One of these, 5-[*N*-(L-phenylalanyl)amino]uridine (PAU), an anti-viral agent, has been studied crystallographically (Berman, Hamilton & Rousseau, 1973) and has demonstrated two kinds of amino acid–nucleic acid base interactions; there were uracil–phenyl group stacking and hydrogen-bonding between the base and the peptide backbone. Another aminoacyl derivative of 5-aminouridine, 5-[*N*-(L-leucyl)amino]uridine (I), also has anti-viral properties.



(I)

As part of a program of study (Berman, Hamilton & Rousseau, 1973; Berman, Zacharias, Carrell & Varghese, 1976; Narayanan, Berman & Rousseau, 1976) to elucidate new amino acid–nucleic acid base interactions, we have determined its crystal structure.