Acta Cryst. (1976). B**32**, 2609

Measurements of Bijvoet Differences. Structure and Absolute Configuration of Africanol, a Sesquiterpene

BY ROLF KARLSSON

*Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-*104 05 *Stockholm, Sweden*

(*Received* 6 *January* 1976; *accepted* 5 *March* 1976)

The structure of africanol, a sesquiterpene from the soft coral *Lemnalia africana*, has been determined by X-ray diffraction. The absolute configuration has been established from nine enantiomer-sensitive Bijvoet differences measured with Cu $K\alpha$ and Cr $K\alpha$ radiations. An analysis of the experimental conditions for adequate measurements of Bijvoet differences is given. The space group of the crystals is $P2_12_12_1$ with $a=24{\cdot}466$ (9), $b=9{\cdot}705$ (1), $c=18{\cdot}064$ (4) Å, with twelve molecules per unit cell. The three independent molecules are associated *via* three hydrogen bonds between the hydroxyl groups into a trimer. Two of the molecules are well related by a non-crystallographic twofold axis in the **a** direction. Freezing-point depression measurements show that the trimer also exists in cyclohexane. The three independent molecules have the same conformation and differ very little with respect to distances and angles.

Introduction

Soft corals have been found to be a rich source of sesqui- and diterpenes (Tursch *et al.*, 1974). Africanol (Fig. 1) and some of its dehydrated forms were extracted from *Lemnalia africana*. Since chemical and spectroscopic investigations did not establish the structure, an X-ray diffraction analysis was undertaken. The structure has been found to have a hitherto unknown skeleton.

Experimental

Africanol crystallizes from methylene chloride in large flakes from which suitable single crystals were cut. Single crystals $2\times10\times10$ mm are not uncommon. They melt at 58–60°, have a very strong odour and are soluble in all common organic solvents. Crystal data are given in Table 1. The density was measured by

Table 1. *Crystal data*

Formula $C_{15}H_{26}O$	$D_m=$ 1·05 g cm^{-3}
Space group $P2_12_12_1$	$D_x=$ 1·030
$a=24{\cdot}466$ (9) Å	$M=$ 222
$b=$ 9·705 (1)	$V=$ 4284 Å^3
$c=18{\cdot}064$ (4)	μ(Cu $K\alpha$) = 4·8 cm^{-1}
$Z=12$	μ(Cr $K\alpha$) = 15·0

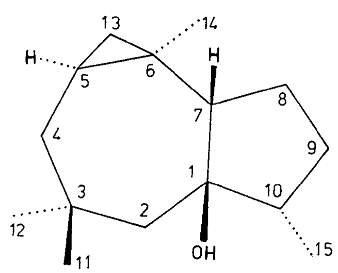

Fig. 1. Africanol, absolute configuration.

flotation in NaI and water in the presence of small amounts of detergent. The space group and refined cell constants were determined, and all data collection performed, with a Philips PW 1100 diffractometer.

Two intensity data sets were collected for half the reciprocal sphere by ω–2θ scans with graphite-monochromatized Cu $K\alpha$ radiation. The first data set was collected from three crystals mounted on glass needles. Since the intensities fell off quite rapidly with increasing Bragg angle, only data to $\theta=50°$ were collected. These data were corrected for the Lp factor and for an intensity decay assumed to be linear in time between successive measurements of three test reflexions. The decay was later shown to be due only to evaporation of the crystal. In the course of the structure solution difficulties were experienced in finding the hydrogen positions. It was then suspected that the intensity loss (being as large as 35%) had affected the quality of the data, despite the corrections applied. A new crystal, a cube of 0·3 mm edge, was enclosed in a glass capillary sealed with epoxy resin to prevent evaporation. A second data set was collected to $\theta<45°$ and averaged to 1981 independent reflexions.

Structure solution and refinement

The structure was solved by use of the convergence method (Germain, Main & Woolfson, 1971) applied to the first data set. The 48 non-hydrogen atoms were refined isotropically by least squares to $R=0{\cdot}19$. A subsequent anisotropic refinement ($R=0{\cdot}18$) showed that the anisotropic contribution to the temperature factors was not significant and a difference map based on anisotropic atoms had no advantage over the one derived from isotropic atoms in revealing hydrogens. Refinements performed with the second data set gave $R=0{\cdot}17$ and a difference map, very similar to the maps from the first data set, showed only 65 of the 78 hydrogens. The C, O and H atoms were refined isotropically by block-diagonal-matrix least squares to $R=0{\cdot}13$, with all structure factor magnitudes assigned equal weight. It was noticed that the observed intensities of strong reflexions were systematically weaker than those calculated. A secondary isotropic extinction correction according to Zachariasen's (1967) formula $F_{corr}=KF_{obs}[1+\beta(\theta)CI_{obs}]$ did improve the agreement between observed and calculated data but not satisfactorily.* The rather low value ($0{\cdot}38\times10^{-6}$) of C was obtained using reflexions with $\theta<25°$, with I_{obs} on an absolute scale and $\beta(\theta)$ equal to 1. The observed, extinction-corrected and calculated structure factors of the three strongest reflexions were for 400: 196, 258, 315; for 203: 185, 229, 339; and for 111: 135, 160, 199.† The reflexions were thus omitted in the recalculation of extinction and all subsequent refinements.

A final refinement of the atomic parameters, including the 62 non-hydroxyl hydrogen atoms found in the difference map, *vs* extinction-corrected data, gave $R=0{\cdot}11$. Final coordinates and thermal parameters for C and O are given in Table 2 and for the 65 H atoms in Table 3. Atomic form factors were calculated for C and O according to Cromer (1968) and for H according to Stewart, Davidson & Simpson (1965).

Table 2. C *and* O *positions* ($\times 10^4$) *and thermal parameters* ($\times 10$ Å^2)

	x	y	z	B
Molecule A				
C(1)	1671 (4)	2260 (10)	249 (5)	40 (2)
C(2)	1615 (4)	845 (12)	−26 (6)	58 (3)
C(3)	1329 (4)	−261 (12)	468 (6)	56 (3)
C(4)	849 (4)	300 (10)	914 (5)	51 (2)
C(5)	432 (4)	1049 (12)	398 (6)	59 (3)
C(6)	597 (4)	2458 (12)	96 (6)	54 (2)
C(7)	1129 (4)	3080 (10)	426 (5)	46 (2)
C(8)	1231 (5)	4566 (13)	151 (7)	68 (3)
C(9)	1863 (5)	4661 (13)	26 (7)	70 (3)
C(10)	2024 (5)	3256 (12)	−247 (6)	57 (3)
C(11)	1741 (5)	−905 (13)	1032 (7)	73 (3)
C(12)	1118 (6)	−1447 (15)	−65 (8)	91 (4)
C(13)	123 (5)	2290 (14)	664 (8)	77 (3)
C(14)	427 (5)	2733 (14)	−680 (7)	77 (3)
C(15)	1929 (5)	3116 (14)	−1062 (7)	80 (3)
O	1984 (3)	2237 (7)	939 (4)	56 (2)
Molecule B				
C(1)	3415 (4)	2117 (10)	1743 (5)	42 (2)
C(2)	3712 (4)	3122 (10)	1231 (5)	44 (2)
C(3)	3696 (4)	4690 (11)	1396 (6)	51 (2)
C(4)	3746 (4)	4973 (12)	2243 (6)	60 (3)
C(5)	4205 (4)	4194 (11)	2603 (6)	57 (3)
C(6)	4167 (4)	2680 (10)	2734 (5)	40 (2)
C(7)	3625 (4)	1999 (10)	2557 (5)	43 (2)
C(8)	3576 (5)	448 (12)	2764 (6)	63 (3)
C(9)	3202 (5)	−184 (14)	2148 (7)	75 (3)
C(10)	3368 (5)	636 (12)	1444 (6)	60 (3)
C(11)	3165 (5)	5370 (13)	1111 (6)	67 (3)
C(12)	4177 (5)	5330 (13)	997 (6)	64 (3)
C(13)	4173 (5)	3650 (12)	3394 (6)	66 (3)
C(14)	4710 (4)	1890 (12)	2637 (6)	65 (3)
C(15)	3900 (5)	92 (14)	1102 (7)	81 (3)
O	2853 (3)	2595 (7)	1829 (3)	53 (1)
Molecule C				
C(1)	1621 (4)	2103 (10)	3226 (5)	41 (2)
C(2)	1653 (4)	3578 (11)	3526 (5)	51 (2)
C(3)	1366 (4)	4710 (12)	3063 (6)	58 (3)
C(4)	833 (4)	4247 (12)	2694 (6)	65 (3)
C(5)	440 (4)	3568 (12)	3262 (6)	57 (3)
C(6)	569 (4)	2106 (12)	3536 (6)	57 (3)
C(7)	1051 (4)	1393 (10)	3152 (5)	45 (2)
C(8)	1140 (5)	−123 (14)	3429 (7)	80 (3)
C(9)	1779 (6)	−301 (15)	3471 (8)	85 (4)
C(10)	1993 (4)	1100 (12)	3684 (6)	61 (3)
C(11)	1747 (5)	5233 (13)	2439 (7)	76 (3)
C(12)	1255 (6)	5958 (15)	3605 (8)	88 (4)
C(13)	79 (5)	2374 (13)	3022 (6)	69 (3)
C(14)	434 (5)	1881 (14)	4334 (7)	75 (3)
C(15)	1982 (6)	1360 (15)	4518 (7)	83 (3)
O	1820 (3)	2069 (7)	2459 (4)	57 (2)

Absolute configuration

The configuration of africanol was determined by the method of Bijvoet, Peerdeman & van Bommel (1951) with Cu $K\alpha$ and Cr $K\alpha$ radiations under the experimental conditions described below. Calculated and observed Bijvoet ratios with standard deviations based on counting statistics are given in Table 4. The dispersion parameters of Cromer & Liberman (1970) were used.

Applications of the Bijvoet method of light-atom structures have been discussed by (*inter alia*) Wetherington, Ament & Moncrief (1974), Hope & de la Camp (1972) and Engel (1972). Adequate Bijvoet differences for the purpose can be obtained if special care is given to adjustment of the diffractometer, selection and mounting of the crystal and the measuring procedure. The author has used the method successfully for four other terpenes.

The instrument

The four-circle diffractometer with normal beam equatorial geometry was used with a flat graphite monochromator with the X-ray beam from the monochromator defining the positive, horizontal x direction. The monochromator is mounted parallel to the y direction. The detector moves in the xy plane. For notations and further information see Arndt & Willis (1966).

*Fine adjustment of the monochromator**

Both reflexions of a Friedel pair will ideally have the same absorption factor if the X-ray beam is sym-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31726 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† No appreciable attenuation in the intensities of the strong reflexions was observed when Mo $K\alpha$ radiation was used; this is in accordance with the theory of primary extinction (Zachariasen, 1945).

* It is assumed that the goniostat and tower angle are properly set.

Table 3. *Hydrogen positions* ($\times 10^3$) *and thermal parameters* ($Å^2$)

	x	y	z	B
Molecule *A*				
H1(C2)	195	49	−22	7
H2(C2)	141	70	−43	5
H1(C4)	92	111	145	3
H(C5)	24	40	−3	11
H(C7)	110	312	113	3
H2(C8)	105	518	54	3
H1(C9)	194	499	−33	13
H2(C9)	206	496	62	4
H(C10)	259	313	−7	2
H1(C11)	179	−36	141	1
H2(C11)	154	−152	134	2
H3(C11)	204	−123	72	1
H1(C12)	144	−172	−27	1
H2(C12)	125	−222	25	8
H3(C12)	76	−125	−37	1
H2(C13)	19	288	111	0
H1(C14)	19	225	−59	10
H2(C14)	49	367	−90	2
H3(C14)	70	226	−103	0
H1(C15)	212	358	−147	10
H2(C15)	205	223	−120	0
H3(C15)	157	303	−124	4
H(O)	179	261	125	0
Molecule *B*				
H1(C2)	351	284	48	11
H2(C2)	400	294	129	1
H1(C4)	336	501	252	4
H2(C4)	372	630	241	8
H(C5)	449	435	241	2
H(C7)	330	247	296	4
H1(C8)	388	−2	272	1
H2(C8)	347	34	347	5
H1(C9)	342	−92	205	2
H2(C9)	280	0	225	2
H(C10)	292	83	88	14
H1(C11)	279	486	119	7
H1(C12)	413	535	41	2
H2(C12)	417	620	111	2
H3(C12)	457	502	101	6
H1(C13)	452	372	370	4
H2(C13)	387	378	358	1
H2(C14)	468	101	282	1
H3(C14)	476	179	202	5
H2(C15)	392	51	60	8
H3(C15)	422	25	136	2
H(O)	247	239	144	10
Molecule *C*				
H2(C2)	153	346	425	7
H1(C4)	90	346	225	4
H2(C4)	66	492	234	5
H(C5)	29	416	377	6
H(C7)	100	140	241	6
H1(C8)	103	3	414	13
H2(C8)	98	−40	297	1
H2(C9)	190	−35	287	1
H(C10)	251	133	345	4
H1(C11)	170	473	194	1
H2(C11)	156	610	215	7
H3(C11)	211	544	262	6
H1(C12)	148	589	397	4
H3(C12)	94	586	405	6
H1(C13)	−36	225	345	10
H2(C13)	5	234	247	1
H1(C14)	8	215	443	9
H2(C14)	46	99	452	1
H3(C14)	75	232	472	2
H(O)	208	195	251	2

Table 4. *Observed* (X_o) *and calculated* (X_c) *Bijvoet ratios* ($\times 100$)

$X_c(\text{Cr }K\alpha) \simeq 2{\cdot}3X_c(\text{Cu }K\alpha)$.

h	k	l	X_c Cu $K\alpha$	X_o Cu $K\alpha$	X_o Cr $K\alpha$
9	1	1	1·3	2·7 (3)	4·0 (5)
11	2	1	0·5	0·8 (2)	2·0 (4)
1	5	1	−1·0	−0·6 (3)	−1·6 (7)
4	5	1	−1·7	−1·2 (5)	
8	1	2	−1·1	−0·9 (3)	−3·6 (9)
2	2	2	−0·6	0·0 (3)	−2·3 (4)
3	4	2	−1·0	−0·7 (4)	
4	1	6	−1·1	−0·6 (3)	−2·3 (4)
4	2	9	0·6	−0·2 (4)	

metric in the xy plane and the crystal is centrosymmetric in shape. For reasons noted later, it is very important for the beam to be symmetric in the xz plane. For adjustment purposes a small crystal of ammonium oxalate (space group $P2_12_12_1$) was cut to a cube of 0·08 mm edge and mounted as described below, approximately in the direction of the c axis. With the very strong 310 reflexion in reflecting position and χ and φ each approximately 0°, the crystal is moved slightly off the centre of the circles at coordinates $(0,0,0)$ by goniometer-head adjustments to $(0,y,z)$. The monochromator is then adjusted to make the integrated intensities at the four positions $(0, \pm y, \pm z)$ the same. The crystal is set to these positions according to the scheme given in Table 5. Since the intensity profile of the beam reflected from the monochromator is rather broad in the y direction, the monochromator is first adjusted so that the beam becomes symmetric around $y=0$. The crystal is then reset to $(0,0,0)$ and the intensity is maximized by changing the monochromator angle θ_m. The intensity profile in the z direction, $I(z)$, is measured with fixed $y=0$ by setting the crystal to successive z values. The profile should be symmetric around its maximum intensity value. In order to obtain the maximum exactly at $z=0$, the crystal is set to a value of z for which $\partial I/\partial z$ is large. θ_m is adjusted so that $I(z)=I(-z)$.

Table 5. *Crystal positions for monochromator adjustments*

hkl	ψ	y	z
h	0	+	+
h	180	+	−
$\bar{h}$	0	−	+
$\bar{h}$	180	−	−

Mounting the crystal

A compact crystal of centrosymmetric shape, about 0·3 mm diameter, was mounted with the aid of micromanipulators on a thin glass pin (0·025 mm) with epoxy resin in such a way as to minimize X-ray shadow from resin and pin. Vibration of the glass fibre was made negligible by affixing it to a thicker glass rod at a point about 0·4 mm below the crystal. To test whether the crystal was properly fixed to the glass pin, a few of the strongest reflexions were set with the ω and 2θ angles to the steepest part of the $I(\theta)$ curve, approximately at half the peak intensity. Stationary measurements were made and it was checked whether successive measurements differed more than was expected from counting statistics.

The measuring procedure

Each reflexion h was measured at the four positions in the symmetrical-A setting given in Table 6 and at all equivalent positions in order to reduce systematic errors. The last three positions in Table 6 are simply obtained by rotating the crystal 180° around the x, y or z axis, with $\omega=0°$. The reflexion $\bar{h}$ is measured after rotating the crystal 180° around the y axis. Dissymmetry in the X-ray beam and miscentring along the y direction will give rise to systematic errors. Measurements of $\bar{h}$ at a negative and a small ω angle will, to some extent, compensate for those errors since the crystal will remain in the same part of the beam as when h is measured. The measurements were made with both Cu $K\alpha$ and Cr $K\alpha$ radiations and usually on the same crystal. It was felt that the measurements with Cr $K\alpha$ radiation were more reliable despite the larger absorption since the dispersion effect is 2·3 times higher than with copper radiation. A serious disadvantage was the long air path of 400 mm between tube and detector, with attendant intensity loss of 80% relative to a path through helium. Reflexions selected for the measurements were mainly those which exhibited large Bijvoet differences, and Bijvoet ratios $2(I_h-I_{\bar{h}})/(I_h+I_{\bar{h}})$ larger than 0·8% (Cu $K\alpha$).

Table 6. *Four angle positions for h in the symmetrical-A setting in normal beam equatorial geometry*

$\omega=\theta$ and $\bar{h}$ is at ω, $-\chi$, $180+\varphi$. Angles are in degrees.

ω	χ	φ	ψ
+	+	+	0
−	180+	+	180
−	−	180+	0
+	180−	180+	180

Discussion

The structure contains three independent molecules (denoted A, B and C) connected *via* their hydroxyl groups by three hydrogen bonds to form the trimer shown in Fig. 2. The molecules A and C are approximately related by a twofold axis through $y=0·78$ and $z=0·175$ in the **a** direction giving rise to a sixteen-fold multiple Patterson vector at ($\frac{1}{2}$,0·06,0·35). Bond distances, bond angles and selected torsion angles are given in Tables 7, 8 and 9. The three molecules have the same conformation with the exception of the OH groups. The seven-membered ring has nearly the twisted-boat conformation (Hendrickson, 1967). The twist conformation of the five-membered ring, with maximum twist around the C(9)–C(10) bond, leads to several short intramolecular contacts (Table 10).

Geometrical calculations showed the hydrogen coordinates in Table 3 to be very inexact; the intensities

Table 7. *Interatomic distances*

The average e.s.d. is 0·012 Å.

	Molecule A	Molecule B	Molecule C
1–2	1·467	1·526	1·533
1–7	1·577	1·559	1·561
1–10	1·576	1·539	1·568
1–O	1·463	1·459	1·465
2–3	1·562	1·550	1·548
3–4	1·523	1·558	1·531
3–11	1·561	1·544	1·544
3–12	1·587	1·510	1·580
4–5	1·559	1·501	1·552
5–6	1·525	1·490	1·534
5–13	1·500	1·523	1·518
6–7	1·552	1·515	1·532
6–13	1·555	1·517	1·535
6–14	1·486	1·544	1·493
7–8	1·544	1·554	1·569
8–9	1·562	1·563	1·572
9–10	1·502	1·554	1·507
10–15	1·493	1·533	1·526

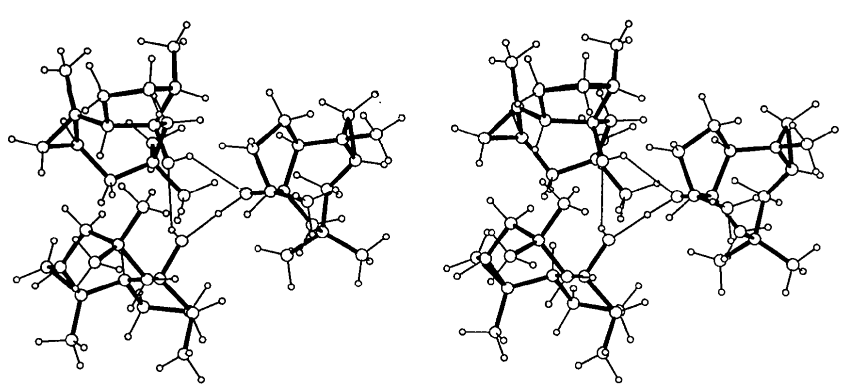

Fig. 2. Africanol, a stereo drawing with hydrogen bonds.

Table 8. *Bond angles* (°)

The average e.s.d. is 0·8°.

	Molecule *A*	Molecule *B*	Molecule *C*
2–1–7	117·6	117·4	119·1
2–1–10	115·6	114·9	111·3
2–1–O	108·8	108·0	109·8
7–1–10	105·4	106·6	106·8
7–1–O	106·0	103·4	101·9
10–1–O	101·9	105·2	107·0
1–2–3	119·4	119·9	116·6
2–3–4	113·4	111·0	114·3
2–3–11	111·1	112·1	110·8
2–3–12	107·2	107·0	106·7
4–3–11	107·2	108·4	107·0
4–3–12	109·3	109·6	110·3
11–3–12	108·4	108·7	107·6
3–4–5	110·8	113·2	111·4
4–5–6	117·3	121·1	118·6
4–5–13	120·8	122·7	119·6
6–5–13	61·9	60·5	60·4
5–6–7	115·6	116·9	115·4
5–6–13	58·3	60·8	59·3
5–6–14	115·1	114·6	113·6
7–6–13	114·4	116·4	113·7
7–6–14	121·7	120·8	122·7
13–6–14	115·6	112·9	115·8
1–7–6	115·5	117·0	116·7
1–7–8	105·6	105·8	105·3
6–7–8	112·1	116·0	112·7
7–8–9	105·2	104·8	104·8
8–9–10	104·6	103·1	105·0
1–10–9	103·0	102·2	102·9
1–10–15	114·7	113·5	114·0
9–10–15	111·5	111·9	113·2
5–13–6	59·8	58·7	60·3

Table 9. *Selected torsion angles* (°)

	Molecule *A*	Molecule *B*	Molecule *C*
7–1–2–3	−61	−65	−63
1–2–3–4	37	40	36
2–3–4–5	53	48	51
3–4–5–6	−74	−73	−75
4–5–6–7	−8	−6	−6
5–6–7–1	65	59	61
6–7–1–2	−16	−11	−12
10–1–7–8	−10	−12	−11
9–10–1–7	31	33	32
8–9–10–1	−41	−42	−39
7–8–9–10	35	35	33
1–7–8–9	−15	−14	−13
H–O–1–7	2	−155	−143
H–O–1–O*C*	−33		
H–O–1–O*A*		0	
H–O–1–O*B*			26

are seriously affected by extinction and thermal effects. Thus the hydrogen positions used for Tables 10, 11 and 12 were calculated with H–C and H–O taken as 1·1 Å and the H–O–C and H–C–H,C angles taken as 109·5°. The methylene groups were assumed to have local C_{2v} symmetry and the CH_3 groups to have staggered positions. However, the C–C–O–H angles in Table 9 are calculated from difference-map hydrogen positions.

Table 10. *Short intramolecular contacts* (Å) (*from calculated hydrogen positions*)

	Molecule *A*	Molecule *B*	Molecule *C*
H2(C2)—H3(C12)	2·32	2·22	2·32
H2(C2)—H3(C14)	2·32	2·45	2·42
H2(C2)—H2(C15)	2·33	2·32	2·20
H1(C4)—H(C7)	2·09	2·19	2·16
H(C5)—H3(C12)	2·11	2·18	2·21
H1(C8)—H2(C14)	2·00	2·14	2·04
H1(C8)—H3(C15)	2·34	2·33	2·48
H1(C11)–O	2·41	2·37	2·34
H3(C14)–H3(C15)	1·98	2·06	2·04
H(C10)—H(O)	–	2·00	2·00
H(C7)—H(O)	1·80	–	–

Intra- and intertrimer distances less than 2·45 Å are given in Tables 11 and 12. The paucity of close contacts may explain the observed high vapour pressure. An examination of the interactions of the C(14) methyl group with neighbouring atoms showed that H must be staggered between C(13) and C(5).

Table 11. *Short intratrimer contacts* (Å)

The last letter in the atomic notation identifies the molecule.

H1(C4)*A*—H(C7)*C*	2·24	H(O*A*)-H(O*C*)	2·47
H(C7)*A*—H1(C4)*C*	2·26	H(O*B*)-H(O*C*)	1·94
H2(C9)*A*—H1(C11)*B*	2·34	H(O*A*)-O*C*	2·07
H2(C13)*A*-H2(C13)*C*	2·26	H(O*B*)-O*A*	1·59
H2(C9)*B*—H2(C9)*C*	2·38	H(O*C*)-O*B*	1·96
H(O*A*)—H1(C11)*C*	2·00	O*A*—O*B*	2·68
H(O*C*)—H2(C9)*B*	2·22	O*A*—O*C*	2·78
H(O*A*)—H(O*B*)	1·86	O*B*—O*C*	2·82

Table 12. *Short intertrimer contacts* (Å)

Molecular notations as in Table 11.

H1(C15)*C*-H1(C2)*A*	2·03
H2(C8)*B*—H2(C2)*A*	2·43
H(C5)*A*—H2(C4)*A*	2·26
H2(C13)*B*-H1(C8)*A*	2·19
H1(C14)*C*-H2(C12)*A*	2·38
H2(C2)*B*—H1(C14)*A*	2·24
H2(C12)*B*-H(C5)*B*	2·19
H3(C15)*C*-H1(C15)*B*	2·37
H2(C12)*C*-H2(C8)*C*	2·30

Information about the hydrogen-bond system is given in Tables 9 and 11 and in Fig. 2. The three O–O distances are different; H(O*A*) lies 0·62Å below the oxygen plane and H(O*B*) and H(O*C*) 0·04 Å above. It is of interest to investigate whether the impediments to a coplanar arrangement of the three OH groups, which would minimize the repulsions between the three hydrogens, are steric or electronic. The H–O–C–O′ angles about C–O bonds, Table 9, indicate how far each H atom lies from its electrostatically most favourable position, *i.e.* in the C–O–O′ plane closest to O′. Thus it is natural that the strongest hydrogen bond, O*B*–O*A*′, has the H–O–C–O′ angle of 0°.

In order to see whether the trimer exists in a preferentially nonpolar solvent, the complex constant for the formation of one mol of trimer was estimated by cryoscopic methods in cyclohexane with only 30 mg compound. The observed value was 1500 (mol fractions). Thus in a solution of 0·01 mol africanol per mol cyclohexane, 11% of the molecules occur as trimers.

The author is indebted to Professor P. Kierkegaard and Professor B. Tursch (Brussels) for their kind interest. The work has been supported by Statens Naturvetenskapliga Forskningsråd. I thank Dr D. F. Koenig for his correction of the English.

References

ARNDT, U. W. & WILLIS, B. T. M. (1966). *Single Crystal Diffractometry*. Cambridge Univ. Press.

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* **168**, 271–272.

CROMER, D. T. (1968). *Acta Cryst.* A**24**, 321–324.

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

ENGEL, D. W. (1972). *Acta Cryst.* B**28**, 1496–1509.

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

HENDRICKSON, J. B. (1967). *J. Amer. Chem. Soc.* **89**, 7036–7061.

HOPE, H. & DE LA CAMP, U. (1972). *Acta Cryst.* A**28**, 201–207.

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

TURSCH, B., BRAEKMAN, J. C., DALOZE, D., FRITZ, P., KELECOM, A., KARLSSON, R. & LOSMAN, D. (1974). *Tetrahedron Lett.* pp. 747–750.

WETHERINGTON, J. B., AMENT, S. S. & MONCRIEF, J. W. (1974). *Acta Cryst.* B**30**, 568–573.

ZACHARIASEN, W. H. (1945). *Theory of X-ray Diffraction in Crystals*, p. 165. New York: John Wiley.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1976). B**32**, 2614

Structures of Nitrogen-Containing Aromatic Compounds. I. The Metastable Crystalline Form of Dibenzo-1,3a,4,6a-tetraazapentalene (DBTAP-2)

BY MICHAEL LAING

Chemistry Department, University of Natal, Durban, South Africa

(*Received* 9 *March* 1976; *accepted* 7 *April* 1976)

The crystalline form of dibenzo-1,3a,4,6a-tetraazapentalene that is metastable at room temperature, DBTAP-2, is monoclinic, $P2_1/c$, $a=6·943$ (5), $b=4·473$ (5), $c=16·11$ (1) Å, $\beta=101·1$ (1)°, $V=491$ Å^3, $Z=2$, $D_m=1·395$ (5) g cm^{-3}. $R=0·059$ for 688 observed data (diffractometer, monochromated Mo $K\alpha$); six C and two N anisotropic, four H's included. The N–N, C–N and C–C lengths are all within 2σ of those in the thermodynamically stable form, DBTAP-1. N(1)–N(1′) 1·368 (10), N(1)–N(2) 1·336 (5), mean C–N 1·383 (5) Å; C–C in the aromatic ring ranges from 1·362 to 1·412 Å. DBTAP-1 changes to DBTAP-2 at 127 °C, which then melts at 237 °C. DBTAP-2 changes to DBTAP-1 merely upon crushing and gentle grinding at room temperature.

Introduction

Dibenzo-1,3a,4,6a-tetraazapentalene (I) was reported to be an unusually stable heteroaromatic compound (Carboni & Castle, 1962); to obtain information about the bond lengths (and, therefore, bond orders), a determination of the crystal structure was undertaken (Burke, 1964). This work showed that two crystalline forms existed: one modification, DBTAP-1, was obtained from $CHCl_3/CCl_4$ solution, the second, DBTAP-2, from CH_3OH. A study was therefore made of the differences between the molecular packing in the two forms (Laing, 1965). Subsequently, a DTA study (Allais, 1966) showed that DBTAP-1 changed to DBTAP-2 at 127 °C and that the melting point reported by Carboni & Castle (1962) is in fact that of DBTAP-2, the form that is metastable at room temperature. The crystal structure of DBTAP-1 has now been reported (Burke Laing, Sparks, Laing & Trueblood, 1976); to obtain a comparison between the bond lengths in the two forms, the structure of DBTAP-2 has been redetermined and refined.

Experimental

Good crystals were obtained with difficulty from a carefully dried methanol solution by evaporation at room temperature. They were parallelepipeds, elongated along [010]. If the methanol was not water-free, the crystals were feathery and consisted of intractable clumps of needles.

Accurate cell dimensions were obtained by a least-squares refinement of 2θ, χ and φ angles for 25 reflexions measured on a Philips four-circle diffractom-