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Structure of an *N*-Monomethylated Cyclic Dipeptide, *cyclo*(-*N*-Methyl-L-phenylalanyl-L-phenylalanyl-)

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Abstract. 1-Methyl-3,6-bis(phenylmethyl)-2,5-piperazinedione, $C_{19}H_{20}N_2O_2$, $M_r = 308{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}254\ (2)$, $b = 13{\cdot}370\ (3)$, $c = 24{\cdot}294\ (4)$ Å, $V = 3330\ (1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}23$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 5{\cdot}6$ cm^{-1}, $F(000) = 1312$, room temperature, $R = 0{\cdot}052$ for 1697 observed reflections. Two crystallographically independent molecules joined through a pair of N–H···O hydrogen bonds form dimers as distinct units in the crystal lattice. The general molecular conformation is similar to that of *cyclo*(L-Phe)$_2$ [Gdaniec & Liberek (1986). *Acta Cryst.* C**42**, 1343–1345]. In molecule *B* the aromatic side chain of the *N*-methylated phenylalanine residue folds over the diketopiperazine moiety [$\chi_1^1 = 61{\cdot}1\ (7)°$] while the other side chain is in extended conformation [$\chi_2^1 = -62{\cdot}5\ (6)°$]. The opposite conformation of the side chains is observed in molecule *A* [$\chi_1^1 = -65{\cdot}9\ (6)$, $\chi_2^1 = 68{\cdot}7\ (6)°$].

Introduction. In the crystal structures of *cyclo*(*N*-Me-L-Phe)$_2$ (Benedetti, Marsh & Goodman, 1976) and *cyclo*(L-Phe)$_2$ (Gdaniec & Liberek, 1986) none of the molecules adopts a conformation with C_2 symmetry postulated on the basis of NMR data (Kopple & Marr, 1967; Deslauries, Grzonka, Schaumburg, Shiba & Walter, 1975). Introduction of a methyl group at one of the 2,5-piperazinedione (hereafter DKP) N atoms destroys the potential symmetry and makes the two phenylalanine residues nonequivalent. ^{1}H NMR data of such monomethylated cyclic dipeptides (Liberek, Bednarek, Kitowska & Macikowska, 1977) speak in favour of a conformation in which the DKP ring is boat, the aromatic ring of the *N*-methylamino-acid residue bends over the DKP nucleus and the other aromatic ring is extended towards the N atom.

The crystal structure of *cyclo*(*N*-Me-L-Phe-L-Phe) has been solved to find out if the preference of an *N*-methylamino-acid residue to fold over the DKP ring is preserved in the solid state as well as to provide more structural data on cyclic dipeptides with two aromtic amino-acid residues.

Experimental. Colourless crystal $0{\cdot}1 \times 0{\cdot}2 \times 0{\cdot}3$ mm from methanol–water, D_m not determined, Syntex $P2_1$ diffractometer, graphite monochromator, lattice parameters from 15 reflections in 2θ 13–22°, profiles measured for 2563 unique reflections with $2\theta \le 115°$ (h 0→11, k 0→14, l 0→26), ω–2θ scan technique, variable scan rate, profile analysis according to Lehmann & Larsen (1974), no significant intensity variation for two standard reflections, absorption ignored, 1697 reflections with $I \ge 1{\cdot}96\sigma(I)$. Structure solved by direct methods with *SHELX*76 (Sheldrick, 1976), full-matrix least-squares refinement on F, $w = 1/\sigma^2$, H atoms bonded to C in calculated positions, H atoms bonded to N located on a ΔF map, final refinement: anisotropic non-H atoms and empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c(1 - xF_c^2/\sin\theta)$, x converged at $1{\cdot}15\ (3) \times 10^{-6}$; $R = 0{\cdot}052$ and $wR = 0{\cdot}046$; $S = 3{\cdot}09$; in final refinement cycle max. $\Delta/\sigma \le 0{\cdot}1$, largest peak in final ΔF map 0·14, largest hole −0·16 e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computer programs: *SHELX*76

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(Sheldrick, 1976), local programs (Jaskólski, 1982), *PLUTO* (Motherwell & Clegg, 1978), *ORTEP* (Johnson, 1976).

Discussion. The final atomic coordinates are given in Table 1, molecular dimensions in Table 2.* Fig. 1 illustrates the conformation of the two independent molecules, *A* and *B*, with atom-numbering scheme.

As in *cyclo*(L-Phe)$_2$ one of the phenylalanyl residues is in a folded and the other in an extended conformation. However, in molecule *B* the aromatic ring of the *N*-methylated amino-acid residue folds over the DKP ring while in molecule *A* the non-methylated residue is in the folded conformation. When adopting the conformation described above, the molecules are able to form dimers through a pair of N–H···O hydrogen bonds (Fig. 2). This type of association is often observed in cyclic dipeptides (Benedetti, Corradini & Pedone, 1969; Gdaniec, 1981; Van Poucke, Geise & Lenstra, 1983).

* Lists of observed and calculated structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43659 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	*y*	*z*	U_{eq}
O(1*A*)	0·3728 (4)	0·2555 (3)	0·4620 (2)	0·077 (2)
O(2*A*)	0·0826 (4)	−0·0411 (3)	0·5419 (2)	0·078 (2)
N(1*A*)	0·2818 (5)	0·0243 (4)	0·5277 (2)	0·059 (2)
N(2*A*)	0·1785 (4)	0·1803 (4)	0·4674 (2)	0·062 (2)
C(*P*1*A*)	0·3044 (6)	0·1835 (5)	0·4763 (3)	0·062 (3)
C(*P*2*A*)	0·1527 (6)	0·0211 (5)	0·5192 (3)	0·060 (3)
C(*A*1*A*)	0·3716 (5)	0·0943 (4)	0·5013 (2)	0·055 (2)
C(*A*2*A*)	0·0911 (6)	0·0997 (5)	0·4824 (3)	0·066 (3)
C(*B*1*A*)	0·4561 (5)	0·0470 (5)	0·4555 (2)	0·067 (2)
C(*B*2*A*)	0·0288 (6)	0·0523 (5)	0·4297 (3)	0·079 (3)
C(*G*1*A*)	0·5537 (6)	−0·0312 (5)	0·4742 (2)	0·057 (2)
C(*G*2*A*)	0·1204 (7)	−0·0048 (6)	0·3935 (3)	0·071 (3)
C(11*A*)	0·6659 (6)	−0·0024 (5)	0·5009 (2)	0·068 (3)
C(21*A*)	0·7550 (7)	−0·0737 (7)	0·5178 (3)	0·086 (3)
C(31*A*)	0·7297 (9)	−0·1738 (6)	0·5080 (3)	0·096 (4)
C(41*A*)	0·6177 (9)	−0·2027 (5)	0·4812 (3)	0·092 (4)
C(51*A*)	0·5309 (6)	−0·1308 (5)	0·4640 (2)	0·071 (3)
C(12*A*)	0·1904 (8)	0·0440 (6)	0·3528 (3)	0·086 (3)
C(22*A*)	0·2768 (8)	−0·0101 (7)	0·3195 (3)	0·096 (4)
C(32*A*)	0·2947 (9)	−0·1099 (7)	0·3284 (3)	0·104 (4)
C(42*A*)	0·2248 (9)	−0·1587 (5)	0·3686 (3)	0·098 (4)
C(52*A*)	0·1404 (7)	−0·1070 (6)	0·4007 (3)	0·081 (3)
C(10*A*)	0·3360 (6)	−0·0489 (5)	0·5681 (2)	0·073 (3)
O(1*B*)	0·4107 (4)	−0·3257 (3)	0·8878 (2)	0·077 (2)
O(2*B*)	0·1117 (6)	−0·6174 (4)	0·8097 (2)	0·108 (2)
N(1*B*)	0·3069 (6)	−0·5407 (5)	0·8082 (2)	0·080 (2)
N(2*B*)	0·2092 (5)	−0·3834 (4)	0·8704 (2)	0·063 (2)
C(*P*1*B*)	0·3367 (7)	−0·3842 (5)	0·8642 (2)	0·064 (3)
C(*P*2*B*)	0·1818 (8)	−0·5445 (6)	0·8193 (3)	0·079 (3)
C(*A*1*B*)	0·3963 (6)	−0·4618 (6)	0·8253 (3)	0·077 (3)
C(*A*2*B*)	0·1173 (6)	−0·4524 (5)	0·8443 (2)	0·067 (2)
C(*B*1*B*)	0·4656 (6)	−0·4079 (6)	0·7766 (3)	0·085 (3)
C(*B*2*B*)	0·0335 (6)	−0·4012 (5)	0·7999 (2)	0·073 (3)
C(*G*1*B*)	0·3747 (7)	−0·3556 (6)	0·7373 (3)	0·074 (3)
C(*G*2*B*)	−0·0531 (6)	−0·3187 (5)	0·8219 (3)	0·064 (3)
C(11*B*)	0·3244 (7)	−0·4072 (6)	0·6923 (3)	0·088 (3)
C(21*B*)	0·241 (1)	−0·3595 (7)	0·6570 (3)	0·109 (4)
C(31*B*)	0·2034 (9)	−0·2626 (7)	0·6651 (3)	0·102 (4)
C(41*B*)	0·2485 (9)	−0·2119 (6)	0·7085 (4)	0·107 (4)
C(51*B*)	0·3373 (8)	−0·2573 (6)	0·7447 (3)	0·092 (4)
C(12*B*)	−0·0262 (7)	−0·2212 (5)	0·8127 (3)	0·081 (3)
C(22*B*)	−0·1049 (7)	−0·1443 (5)	0·8332 (3)	0·091 (3)
C(32*B*)	−0·2122 (7)	−0·1676 (7)	0·8633 (3)	0·085 (3)
C(42*B*)	−0·2427 (8)	−0·2638 (7)	0·8725 (3)	0·105 (4)
C(52*B*)	−0·1632 (7)	−0·3394 (6)	0·8521 (3)	0·093 (3)
C(10*B*)	0·3671 (8)	−0·6308 (6)	0·7833 (3)	0·115 (4)

Table 2. *Molecular dimensions*

	Molecule *A*	Molecule *B*
(*a*) Bond lengths (Å)		
C(*P*1)–O(1)	1·240 (8)	1·232 (8)
C(*P*1)–N(2)	1·310 (8)	1·316 (8)
C(*P*1)–C(*A*1)	1·506 (9)	1·531 (10)
C(*A*1)–N(1)	1·461 (7)	1·459 (10)
C(*A*1)–C(*B*1)	1·546 (8)	1·556 (10)
C(*B*1)–C(*G*1)	1·517 (8)	1·507 (10)
C(*G*1)–C(11)	1·377 (8)	1·391 (10)
C(*G*1)–C(51)	1·374 (9)	1·381 (12)
C(11)–C(21)	1·383 (10)	1·367 (12)
C(21)–C(31)	1·383 (12)	1·366 (13)
C(31)–C(41)	1·375 (12)	1·336 (12)
C(41)–C(51)	1·375 (11)	1·405 (12)
N(1)–C(10)	1·494 (8)	1·482 (10)
C(*P*2)–O(2)	1·230 (8)	1·233 (10)
C(*P*2)–N(1)	1·341 (8)	1·312 (10)
C(*P*2)–C(*A*2)	1·518 (9)	1·523 (10)
C(*A*2)–N(2)	1·448 (8)	1·464 (8)
C(*A*2)–C(*B*2)	1·563 (9)	1·539 (9)
C(*B*2)–C(*G*2)	1·497 (10)	1·513 (9)
C(*G*2)–C(12)	1·386 (10)	1·351 (10)
C(*G*2)–C(52)	1·392 (11)	1·374 (10)
C(12)–C(22)	1·401 (12)	1·398 (10)
C(22)–C(32)	1·364 (14)	1·358 (10)
C(32)–C(42)	1·375 (12)	1·343 (13)
C(42)–C(52)	1·355 (11)	1·389 (11)
(*b*) Bond angles (°)		
N(2)–C(*P*1)–C(*A*1)	119·5 (5)	118·2 (5)
N(2)–C(*P*1)–O(1)	122·4 (5)	123·6 (5)
C(*A*1)–C(*P*1)–O(1)	118·0 (5)	118·2 (5)
C(*P*1)–C(*A*1)–C*B*1)	106·9 (4)	109·8 (5)
C(*P*1)–C(*A*1)–N(1)	113·3 (4)	114·5 (5)
N(1)–C(*P*2)–C(*A*2)	118·7 (5)	118·4 (6)
N(1)–C(*P*2)–O(2)	121·9 (5)	124·1 (6)
N(1)–C(*A*1)–C(*B*1)	114·0 (5)	113·9 (6)
N(2)–C(*A*2)–C(*B*2)	110·4 (5)	112·5 (5)
C(*A*2)–C(*P*2)–O(2)	119·3 (5)	117·4 (6)
C(*P*2)–C(*A*2)–C(*B*2)	111·8 (5)	108·9 (5)
C(*P*2)–C(*A*2)–N(2)	114·0 (5)	113·7 (4)
C(*A*1)–N(1)–C(*P*2)	125·1 (4)	125·7 (6)
C(*A*2)–N(2)–C(*P*1)	126·3 (5)	125·8 (5)
C(*A*1)–C(*B*1)–C(*G*1)	115·8 (4)	114·5 (5)
C(*A*2)–C(*B*2)–C(*G*2)	115·6 (5)	114·0 (5)
C(*B*1)–C(*G*1)–C(11)	120·0 (5)	119·8 (6)
C(*B*2)–C(*G*2)–C(12)	120·3 (6)	121·7 (6)
C(*B*1)–C(*G*1)–C(51)	120·1 (5)	122·0 (6)
C(*B*2)–C(*G*2)–C(52)	121·3 (6)	121·6 (5)
C(51)–C(*G*1)–C(11)	119·9 (5)	118·2 (6)
C(52)–C(*G*2)–C(12)	118·4 (6)	116·7 (6)
C(*G*1)–C(11)–C(21)	119·9 (6)	119·5 (6)
C(*G*2)–C(12)–C(22)	119·8 (6)	122·2 (6)
C(11)–C(21)–C(31)	119·5 (7)	122·0 (7)
C(12)–C(22)–C(32)	119·9 (7)	119·4 (6)
C(21)–C(31)–C(41)	120·6 (7)	119·8 (7)
C(22)–C(32)–C(42)	120·4 (7)	119·9 (7)
C(31)–C(41)–C(51)	119·2 (7)	119·9 (7)
C(32)–C(42)–C(52)	120·0 (7)	120·0 (7)
C(41)–C(51)–C(*G*1)	120·8 (6)	119·7 (8)
C(42)–C(52)–C(*G*2)	121·5 (6)	121·8 (6)
C(*A*1)–N(1)–C(10)	118·3 (4)	116·3 (5)
C(*P*2)–N(1)–C(10)	116·6 (4)	117·4 (6)
(*c*) Torsion angles (°)		
C(*A*1)–N(1)–C(*P*2)–C(*A*2)	−4·4 (7)	10·3 (7)
C(*A*2)–N(2)–C(*P*1)–C(*A*1)	4·2 (7)	1·7 (7)
C(*P*2)–N(1)–C(*A*1)–C(*P*1)	17·6 (6)	6·4 (8)
C(*P*1)–N(2)–C(*A*2)–C(*P*2)	9·6 (7)	14·6 (7)
N(2)–C(*P*1)–C(*A*1)–N(1)	−17·2 (6)	−12·6 (6)
N(1)–C(*P*2)–C(*A*2)–N(2)	−9·4 (6)	−20·2 (6)
N(1)–C(*A*1)–C(*B*1)–C(*G*1)	−65·9 (6)	61·1 (7)
N(2)–C(*A*2)–C(*B*2)–C(*G*2)	68·7 (6)	−62·5 (6)
C(*A*1)–C(*B*1)–C(*G*1)–C(11)	−74·8 (6)	−89·5 (7)
C(*A*2)–C(*B*2)–C(*G*2)–C(12)	−87·3 (7)	106·3 (7)
C(*A*1)–C(*B*1)–C(*G*1)–C(51)	105·7 (6)	89·6 (8)
C(*A*2)–C(*B*2)–C(*G*2)–C(52)	90·8 (7)	−73·8 (7)

One of the aspects of cyclic dipeptide structures is the conformation of the DKP ring. The planarity of the *cis* peptide bond makes the boat or planar conformation of the DKP ring most probable. However, steric interactions between substituents on DKP as well as some deviations from 0° of the peptide ω torsion angle (torsion-angle nomenclature according to IUPAC–IUB Commission on Biochemical Nomenclature, 1970) give rise to other types of ring buckling. In *cyclo*(L-Phe)$_2$, where both peptide bonds are planar, the DKP ring takes the form of a flattened boat $B_{C_1^a,C_2^a}$ (notation proposed by Boyens, 1978) with C$^\beta$ atoms in pseudo-axial positions. Substitution of the piperazine N atoms with alkyl groups introduces some strain to the molecule and flattens the potential-energy minimum about the planar conformation of the peptide group. This, in consequence, allows for larger deviations from 0° of the ω torsion angle (Benedetti *et al.*, 1976). In *cyclo*(*N*-Me-L-Phe)$_2$ the ω torsion angles have values of -14 and $-7°$ and the DKP ring takes the form of a twisted boat ${}^{N_2}T_{C_1^a}$ (Benedetti *et al.*, 1976). In the present *cyclo*(*N*-Me-L-Phe-L-Phe) with only one tertiary N atom present, two different types of conformation of the DKP ring are observed. From the Cremer & Pople (1975) puckering parameters (Table 3) it can be inferred that in molecule *A* [$\omega_1 = -4{\cdot}4\,(7)$, $\omega_2 = 4{\cdot}2\,(7)°$] the central ring takes a form intermediate between boat $B_{C_1^a,C_2^a}$ and envelope $E_{C_1^a}$ with C$^\beta$ pseudoaxial while in molecule *B* where the ω angle of the methylated peptide unit is 10·3 (7)° and the other peptide unit is planar [$\omega_2 = 1{\cdot}7\,(7)°$] the conformation is intermediate between twist boat ${}^{C_2'}T_{C_1^a}$ and boat $B_{C_1^a,C_2^a}$.

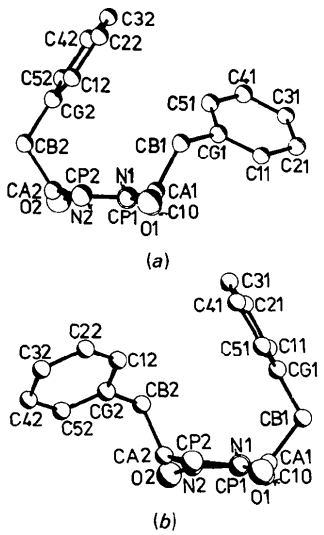

Fig. 1. Conformation of the *cyclo*(*N*-Me-L-Phe-L-Phe) molecules viewed along N(2)–C(*P*2). (*a*) Molecule *A*; (*b*) molecule *B*.

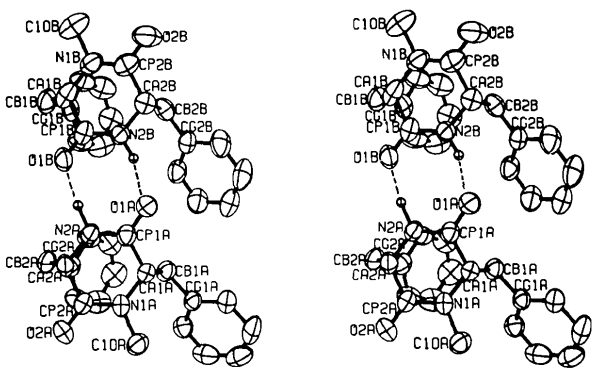

Fig. 2. Stereoview of the *cyclo*(*N*-Me-L-Phe) dimer; dashed lines show the N–H···O hydrogen bonds [O(1*A*)···N(2B^i) 2·930 (6) Å, N(2*A*)···O(2B^i) 2·889 (7) Å; (i): $0{\cdot}5 - x$, $-y$, $-0{\cdot}5 + z$].

Table 3. *The Cremer & Pople (1975) puckering parameters of the DKP ring*

The sequence C(1*P*), C(1*A*), N(1), C(2*P*), C(2*A*), N(2) is used.

	Molecule *A*	Molecule *B*
q_2 (Å)	0·183 (7)	0·199 (4)
q_3 (Å)	0·035 (6)	−0·035 (4)
Q (Å)	0·186 (7)	0·202 (4)
φ_2 (°)	58 (2)	40 (1)
θ_2 (°)	79 (2)	100 (1)

Another interesting feature of the *cyclo*(*N*-Me-L-Phe-L-Phe) structure is the distance of one of the methylene protons of the Phe residue in extended conformation to the mean plane through the phenyl ring of the second residue (in folded conformation). The distance is very similar in molecule *A* (2·60 Å) and molecule *B* (2·68 Å) and in *cyclo*(L-Phe)$_2$ (2·62 Å) and may indicate that there is some kind of interaction between the methylene proton and the π electron cloud of the phenyl ring.

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Structure of the 2,5-Dimethyl Ether of Avarol,* a Sesquiterpenoid Hydroquinone from the Marine Sponge *Dysidea avara*

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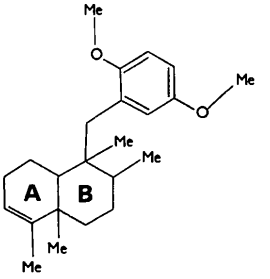
Abstract. $C_{23}H_{34}O_2$, $M_r = 342{\cdot}53$, monoclinic, $P2_1$, $a = 17{\cdot}200\ (9)$, $b = 6{\cdot}599\ (4)$, $c = 19{\cdot}316\ (12)$ Å, $\beta = 111{\cdot}67\ (4)°$, $V = 2037\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}12$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu(\text{Cu } K\alpha) = 0{\cdot}50$ mm^{-1}, $F(000) = 752$, room temperature, final $R = 0{\cdot}056$ for 2825 independent observed reflections and 451 parameters. The two independent molecules in the asymmetric unit show identical features except for the different orientation of the hydroquinone fragment with respect to the C_{15} sesquiterpene moiety, due to crystal packing requirements. Of the two *trans*-connected six-carbon-atom rings forming the sesquiterpene system the cyclohexene ring *A* has a conformation intermediate between the sofa and half-chair forms, while the cyclohexane ring *B* shows a slightly distorted chair conformation.

Introduction. The title compound is the 2,5-dimethyl ether of avarol, a sesquiterpenoid hydroquinone extracted from the sponge *Dysidea avara* (Minale, Riccio & Sodano, 1974). Its absolute stereochemistry has been stated by De Rosa, Minale, Riccio & Sodano (1976) by spectroscopic and chemical methods. Some doubts about the correctness of these assignments were raised by Djura, Stierle, Sullivan, Faulkner, Arnold & Clardy (1980), owing to the inconsistency of physical data reported for a reaction product common to two different chemical pathways starting from avarol and aureol. Recently, Cariello, De Nicola Giudici & Zanetti (1980) have reported that avarol is active in inducing development aberrations in sea-urchin eggs.



Experimental. Needle-shaped crystal (from ethanol), elongated along **b**, $0{\cdot}5 \times 0{\cdot}12 \times 0{\cdot}12$ mm, Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation, cell dimensions determined by a least-squares procedure applied to the setting angles of 20 reflections in the θ range $10 \le \theta \le 13°$. 2825 unique observed reflections [$I_o > 3\sigma(I_o)$] out of the total 3784 measured by the ω/θ scan technique with $\theta \le 65°$, $0 \le h \le 19$, $0 \le k \le 7$, $-21 \le l \le 21$. Three monitoring reflections, intensity variation < 4%. Lp correction, absorption ignored. Structure solved by direct methods: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least squares

* Avarol = [1*R*(1α,2β,4aβ,8aβ)]-2-[(1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-1-naphthalenyl)methyl]-1,4-benzenediol.

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