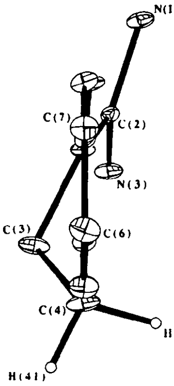


Fig. 3. View of the debrisoquin cation looking edge on to the ring system with the delocalized ring in the foreground. For clarity, thermal ellipsoids are drawn at the 10% probability level and only a few of the atoms are labelled. Only the H atoms on C(4) are shown.

We are grateful to Dr M. S. Lennard (Sheffield, England) for supplying debrisoquinium sulfate and to Professor M. B. Hursthouse (Cardiff, Wales) for the use of his data-collection facilities.

References

Budavari, S., O'Neil, M. J., Smith, A. & Heckelman, P. E. (1989). Editors. *The Merck Index. An Encyclopedia of Chemicals, Drugs, and Biologicals.* Rathway, NJ: Merck & Co., Inc.

Eichelbaum, M., Bertilsson, L., Kupfer, A., Steiner, E. & Meese, C. O. (1988). *Br. J. Clin. Pharmacol.* **25**, 505–508.

Islam, S. A., Wolf, C. R., Lennard, M. S. & Sternberg, M. J. E. (1991). *Carcinogenesis*, **12**, 2211–2219.

Lennard, M. S. (1990). *Pharmacol. Toxicol.* **67**, 273–283.

Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES*, Version 11-Sep-1989. Distributed by Enraf-Nonius, Delft, The Netherlands.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Wolf, C. R. (1986). *Trends Genet.* **2**, 209–214.

Acta Cryst. (1993). C**49**, 303–307

Structures of Derivatives of the Diels–Alder Adduct 1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-9,10-anthraquinone

By Gilroy Alex and S. Srinivasan

Department of Physics, Indian Institute of Technology, Madras 600 036, *India*

R. Bakthavatchalam and S. R. Ramadas

Department of Chemistry, Indian Institute of Technology, Madras 600 036, *India*

and Babu Varghese

Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras 600 036, *India*

(*Received* 30 *July* 1991; *accepted* 22 *July* 1992)

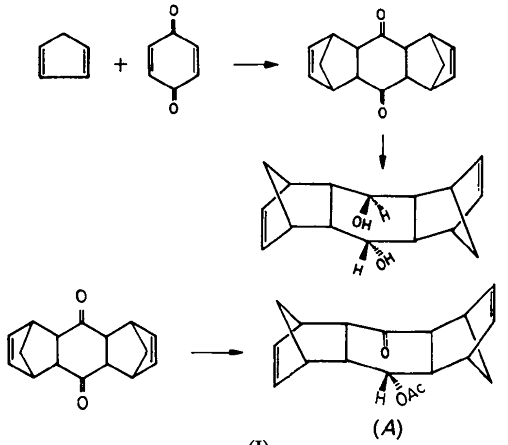
Abstract. 1,4,4a,5,8,8a,9,9a,10,10a-Decahydro-10-oxo-1,4:5,8-dimethanoanthracen-9-yl acetate (*A*), $C_{18}H_{20}O_3$, $M_r = 284.37$, orthorhombic, *Pbca*, $a = 12.036$ (3), $b = 28.753$ (3), $c = 8.451$ (3) Å, $V = 2924.96$ Å^3, $Z = 8$, $D_m = 1.28$ (4), $D_x = 1.296$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.081$ mm^{-1}, $F(000) = 1216$, $T = 293$ K, $R = 0.054$, $wR = 0.057$ for 1207 reflections. (1aα,2β,2aβ,3α,3aα,4α,4aβ,5aβ,6α,6aα,7α,7aβ,8β,8aα)-Tetradecahydro-7-hydroxy-2,8:4,6-dimethanoanthra[2,3-*b*:6,7-*b*′]bisoxiren-3-yl acetate (*B*), $C_{18}H_{22}O_5$, $M_r = 318.37$, monoclinic, $P2_1/c$, $a = 8.741$ (1), $b = 20.477$ (2), $c = 9.890$ (1) Å, $\beta = 92.17$ (1)°, $V = 1768.93$ Å^3, $Z = 4$, $D_m = 1.18$ (3), $D_x = 1.195$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 0.677$ mm^{-1}, $F(000) = 680$, $T = 293$ K, $R = 0.023$, $wR = 0.029$ for 2141 reflections. The central ring and the two terminal six-membered rings of the polycycle adopt distorted boat conformations in both derivatives. The stereochemistry of the polycycle is *endo*, *cis*, *anti*, *cis*, *endo*. The packing of the molecules in (*B*) is in the form of parallel chains with the weak interchain linkage being consistent with the poor shear strength of its crystals.

Introduction. Polycyclic polyfunctional compounds are known to be useful as curing agents for polyurethanes containing —NCO as terminal groups. These polyurethanes are extensively employed in space applications (Robbins, 1970). Bakthavatchalam (1987) synthesized a number of polyfunctional compounds using the Diels–Alder adduct 1,4,4a,5,8,8a,9a,10a-octahydro-1,4:5,8-dimethano-9,10-anthraquinone as starting material. The two compounds

© 1993 International Union of Crystallography

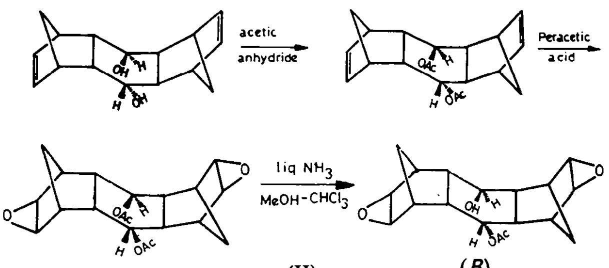
reported here are among these derivatives. The structure analysis was undertaken to determine the stereochemistry of the polycyclic system.

Experimental. The Diels–Alder adduct was prepared by keeping a mixture of cyclopentadiene and freshly sublimed *p*-benzoquinone in 5:1 molar ratio in the dark for 24 h, followed by removal of volatile materials by evaporation under reduced pressure and recrystallization of the residue from benzene. Reduction of the carbonyl function of the adduct with alkaline sodium borohydride in methanol at room temperature followed by recrystallization gave two isomeric diols, one of which was insoluble in methanol. The soluble diol was removed from the mother liquor and recrystallized from benzene and identified as 1,4,4a,5,8,8a,9,9a,10,10a-decahydro-1,4:5,8-dimethanoanthracene-9,10-diol [see (I) below].



(I)

Partial reduction of the Diels–Alder adduct with $NaBH_4$ gave the monoketoalcohol, which, on treatment with acetic anhydride and pyridine gave the ketoacetate (*A*). The diol was heated with acetic anydride containing a few drops of pyridine at 403 K to give the diacetate. This, when reacted with peracetic acid at room temperature yielded the epoxide diacetate, which on treatment with liquid ammonia in MeOH–$CHCl_3$ (5:1) at room temperature gave (*B*) as one of the products [see (II) below].



(II)

Table 1. *Crystal data and X-ray structure determination parameters*

	Compound (*A*)	Compound (*B*)
Crystal dimensions (mm)	0.60 × 0.40 × 0.30	0.55 × 0.20 × 0.10
$\vert h\vert$, $\vert k\vert$, $\vert l\vert$ ranges	15, 27, 10	6, 20, 12
Reflections monitored	1,3,12, 453	224, $\bar{2}24$
Number of reflections	2034	2944
Number of reflections with $I > 3\sigma(I)$	1207	2141
$2\theta_{max}$ (°)	51	70
R_{int}	0.060	0.030
R_σ	0.028	0.025
$(Shift/e.s.d.)_{max}$	0.007	0.121
Max., min. heights in final difference map (e Å^{-3})	0.237, −0.257	0.259, −0.136

It was isolated on the basis of its solubility in methanol and recrystallized yielding colourless needle-shaped crystals.

The crystal data and the X-ray structure determination parameters are given in Table 1. The unit-cell parameters were refined on the basis of 20 2θ values [$20 < 2\theta < 40°$ for (*A*) and $50 < 2\theta < 70°$ for (*B*)]. No significant change in the intensity of check reflections monitored every 100 reflections was observed. Lp corrections were made, but absorption was neglected.

All data were collected on an Enraf–Nonius CAD-4 diffractometer with a graphite-crystal monochromator. The program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) was used for structure solution and the program *SHELX*76 (Sheldrick, 1976) was used for structure refinement. Weighting scheme $w = k\{[\sigma(F_o)]^2 + g(|F_o|)^2\}^{-1}$ with $k = 1.0000/0.7566$ and $g = 0.023012/0.000635$ for (*A*)/(*B*). Quantity minimized: $\sum w(|F_o| - k|F_c|)^2$. Atomic scattering factors from *SHELX*76 (Sheldrick, 1976). Calculations on a Siemens 7580-E system.

Discussion. The final atomic coordinates are listed in Tables 2* and 3 for (*A*) and (*B*), respectively. The *ORTEP* plots (Johnson, 1965) of the molecules of (*A*) and (*B*) are given in Figs. 1 and 2, respectively. Bond lengths, bond angles and selected torsion angles of both compounds are given in Table 4.

The Diels–Alder adduct (Brown, Bruce, Hudson & Mills, 1974) and its two derivatives are found to share the following features with respect to bond lengths and angles: (i) the C(sp^3)—C(sp^3) bond lengths at the ring junctions are invariably longer than the other C(sp^3)—C(sp^3) bond lengths and (ii) the bond angles at the methylene bridges are significantly lower (ranging from 91.4 to 94.2°) than the

---

* Lists of structure factors, anisotropic thermal parameters, intermolecular non-bonded distances and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55608 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0067]

Table 2. *Final positional parameters* ($\times 10^4$ *for non-*H *atoms and* $\times 10^3$ *for* H *atoms) and isotropic or equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for compound* (*A*)

For non-H atoms $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

	x	y	z	U_{iso}/U_{eq}
O(1)	8405 (2)	4366 (1)	1899 (4)	59 (2)
O(2)	9460 (2)	2700 (1)	−485 (3)	58 (2)
O(3)	10014 (4)	4547 (2)	2935 (6)	131 (3)
C(1)	7340 (3)	2827 (1)	1976 (5)	52 (2)
C(2)	6513 (3)	3072 (2)	916 (5)	52 (2)
C(3)	6414 (3)	3500 (2)	1470 (5)	55 (2)
C(4)	7158 (3)	3549 (2)	2893 (5)	50 (2)
C(4a)	8394 (3)	3543 (1)	2366 (4)	41 (2)
C(5)	9185 (3)	4187 (2)	−1593 (5)	56 (3)
C(6)	10368 (3)	4009 (2)	−1389 (6)	63 (2)
C(7)	10430 (3)	3590 (2)	−1999 (5)	62 (2)
C(8)	9301 (3)	3468 (2)	−2616 (4)	56 (2)
C(8a)	8537 (3)	3396 (1)	−1134 (4)	40 (2)
C(9)	8896 (3)	3022 (1)	−18 (4)	39 (2)
C(9a)	8531 (3)	3045 (1)	1673 (4)	41 (2)
C(10)	8814 (3)	3924 (1)	1291 (4)	40 (2)
C(10a)	8448 (3)	3896 (1)	−439 (4)	43 (2)
C(11)	7081 (3)	3057 (2)	3572 (5)	59 (2)
C(12)	8898 (4)	3946 (2)	−3163 (5)	66 (2)
C(13)	9057 (4)	4630 (2)	2791 (5)	62 (2)
C(14)	8457 (5)	5019 (2)	3556 (8)	85 (3)
H(1)	738 (3)	248 (2)	189 (4)	71 (11)
H(2)	618 (3)	290 (1)	−6 (5)	68 (11)
H(3)	602 (3)	377 (1)	106 (4)	56 (9)
H(4)	696 (2)	378 (1)	353 (4)	37 (7)
H(4a)	886 (3)	357 (1)	332 (4)	52 (9)
H(5)	905 (4)	455 (2)	−142 (6)	108 (14)
H(6)	1092 (4)	418 (2)	−87 (5)	71 (12)
H(7)	1105 (3)	338 (1)	−187 (5)	65 (11)
H(8)	929 (3)	321 (1)	−342 (4)	48 (9)
H(8a)	780 (2)	328 (1)	−153 (4)	32 (7)
H(9a)	910 (3)	286 (1)	224 (4)	37 (7)
H(10)	960 (3)	392 (1)	141 (4)	23 (7)
H(10a)	769 (3)	401 (1)	−54 (5)	63 (10)
H(11.1)	631 (3)	298 (1)	402 (5)	68 (11)
H(11.2)	762 (4)	294 (2)	457 (6)	132 (16)
H(12.1)	933 (4)	407 (2)	−412 (5)	96 (14)
H(12.2)	820 (4)	397 (2)	−339 (6)	86 (13)
H(14.1)	904 (4)	522 (2)	426 (8)	145 (32)
H(14.2)	782 (4)	488 (2)	431 (6)	235 (67)
H(14.3)	810 (4)	524 (2)	266 (5)	108 (24)

Table 3. *Final positional parameters* ($\times 10^4$) *and isotropic or equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for compound* (*B*)

For non-H atoms $U_{eq} = (1/3)[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$.

	x	y	z	U_{iso}/U_{eq}
O(1)	2980 (1)	4469 (1)	−127 (1)	49 (1)
O(2)	4713 (1)	6386 (1)	3069 (1)	49 (1)
O(3)	5218 (1)	6817 (1)	1088 (1)	47 (1)
O(4)	−1199 (1)	5351 (1)	2971 (1)	48 (1)
O(5)	1260 (1)	6236 (1)	6691 (1)	51 (1)
C(1a)	3481 (2)	5031 (1)	646 (1)	47 (1)
C(2)	4113 (2)	4940 (1)	2132 (1)	54 (1)
C(2a)	3170 (2)	5423 (1)	3029 (1)	48 (1)
C(3)	3198 (2)	6121 (1)	2569 (1)	52 (1)
C(3a)	2016 (2)	6578 (1)	3076 (1)	51 (1)
C(4)	2081 (2)	6796 (1)	4632 (1)	51 (1)
C(4a)	2201 (2)	6158 (1)	5475 (1)	47 (1)
C(5a)	573 (2)	5982 (1)	5412 (1)	48 (1)
C(6)	−329 (2)	6415 (1)	4355 (1)	49 (1)
C(6a)	373 (2)	6305 (1)	2920 (1)	50 (1)
C(7)	223 (2)	5599 (1)	2470 (1)	51 (1)
C(7a)	1510 (2)	5132 (1)	2929 (1)	48 (1)
C(8)	1662 (2)	4517 (1)	1996 (1)	48 (1)
C(8a)	1841 (2)	4851 (1)	578 (1)	49 (1)
C(9)	3308 (2)	4287 (1)	2484 (1)	52 (1)
C(10)	467 (2)	7054 (1)	4806 (1)	51 (1)
C(11)	5527 (2)	6741 (1)	2253 (1)	47 (1)
C(12)	6832 (2)	7036 (1)	3027 (1)	48 (1)
H	−1041 (20)	4903 (8)	3219 (17)	53 (5)
H(1a)	4228 (20)	5425 (8)	367 (17)	50 (5)
H(2)	5024 (43)	4958 (18)	2553 (39)	149 (14)
H(2a)	3624 (26)	5516 (10)	3973 (21)	78 (7)
H(3)	2911 (22)	6125 (9)	1416 (18)	57 (5)
H(3a)	2256 (22)	6994 (8)	2436 (18)	56 (5)
H(4)	3045 (26)	7145 (10)	4910 (21)	79 (7)
H(5a)	−171 (24)	5513 (9)	5222 (19)	63 (6)
H(6a)	−192 (23)	6515 (9)	2041 (18)	64 (6)
H(7)	321 (26)	5603 (11)	1262 (22)	80 (7)
H(7a)	987 (24)	5025 (10)	3977 (20)	63 (6)
H(8)	675 (25)	4124 (10)	2001 (20)	73 (6)
H(9.1)	3426 (23)	4188 (8)	3536 (19)	58 (5)
H(9.2)	3718 (24)	3890 (10)	1946 (20)	73 (6)
H(12.1)	7506 (21)	7328 (8)	2352 (17)	53 (5)
H(12.2)	7635 (27)	6635 (11)	3579 (23)	71 (7)
H(12.3)	6384 (24)	7327 (10)	3746 (19)	68 (6)
H(4a)*	3341	5945	5332	
H(6)*	−1580	6361	4303	
H(8a)*	734	5072	290	
H(10.1)*	255	7187	5844	
H(10.2)*	185	7465	4155	

* Fixed from stereochemical considerations.

ideal tetrahedral angle. This has been observed for the methylene bridges of other compounds, for example, in the methylene bridges of the norbornene moiety in 1-methyl-3-oxotricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-6-carboxylic acid and 5-methyl-3-oxotricyclo[5.2.1.$0^{2,6}$]dec-8-ene-6-carboxylic acid (Watson, Nagl, Kashyap, Marchand & Vidyasagar, 1990).

In both compounds, the central six-membered ring and the terminal rings adopt distorted boat conformations with varying degrees of distortion, quantified by the asymmetry parameters ΔC_s at their flagpole atoms (Duax & Norton, 1975): 3.6 (2) at C(1), 3.9 (3) at C(10) and 3.4 (3)° at C(5) in (*A*) and 8.3 (3) at C(2), 3.6 (3) at C(7) and 9.1 (3)° at C(4) in (*B*).

The low values of the torsion angles (Table 4) involving the H atoms at the ring junctions and the C atoms of the central ring confirm the *cis* and *anti* characters of these substituents in (*A*) and (*B*). The methylene bridges of both terminal rings point away from the central ring in both compounds (Figs. 1 and 2) leading to their *endo*, *endo* nature. These conclusions are in agreement with the stereochemistry of the adduct (Brown *et al.*, 1974) and three other derivatives of the same adduct solved recently: tetradecahydro-2,4:6,8-dimethanooxireno[4′,5′]benz[1′,2′:5,6]indeno[7,1-*bc*]furan-5,10-diyl diacetate, (Engel, 1988), 2a,3,4,4a,5a,6,9,9a,9b,9c-decahydro-2,4:6,9-dimethanobenz[5,6]indeno[7,1-*bc*]furan-5(2*H*)-one (Engel, 1988) and (1aα,2β,2aβ,3α,3aα,4α,4aβ,5aβ,6α,6aα,7α,7aβ,8β,8aα)-tetradecahydro-2,8:4,6-dimethanoanthra[2,3-*b*:6,7-*b*′]bisoxirene-3,7-diol monohydrate (Ganesh, Varghese, Seshasayee, Bakthavatchalam & Ramadas, 1989).

The intermolecular contact distances between adjacent members of a chain are normal, those between adjacent chains are unusually large, the shortest contact distance being 4.123 Å between C(12) (x, y, z) and O(1) ($x, \frac{1}{2} - y, \frac{1}{2} + z$ with translation 021). This is reflected in the poor mechanical strength of its crystals, which bent at the slightest application of force during mounting for data collection.

Table 4. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *of compounds* (*A*) *and* (*B*)

Compound (*A*)

O(1)—C(10)	1.456 (4)	C(5)—C(6)	1.523 (6)
O(1)—C(13)	1.327 (6)	C(5)—C(10a)	1.561 (6)
O(2)—C(9)	1.214 (4)	C(5)—C(12)	1.536 (6)
O(3)—C(13)	1.183 (7)	C(6)—C(7)	1.312 (8)
C(1)—C(2)	1.513 (6)	C(7)—C(8)	1.497 (5)
C(1)—C(9a)	1.585 (5)	C(8)—C(8a)	1.568 (5)
C(1)—C(11)	1.534 (6)	C(8)—C(12)	1.529 (8)
C(2)—C(3)	1.322 (8)	C(8a)—C(9)	1.494 (4)
C(3)—C(4)	1.506 (6)	C(8a)—C(10a)	1.557 (4)
C(4)—C(4a)	1.553 (5)	C(9)—C(9a)	1.496 (5)
C(4)—C(11)	1.527 (8)	C(10)—C(10a)	1.529 (5)
C(4a)—C(9a)	1.556 (4)	C(13)—C(14)	1.480 (8)
C(4a)—C(10)	1.510 (4)		

O(1)—C(10)—C(4a)	107.9 (2)	C(4a)—C(4)—C(11)	99.0 (3)
O(1)—C(10)—C(10a)	106.6 (2)	C(4a)—C(9a)—C(9)	115.6 (3)
C(10)—O(1)—C(13)	120.0 (3)	C(9a)—C(4a)—C(10)	113.9 (3)
O(1)—C(13)—O(3)	121.3 (4)	C(4a)—C(10)—C(10a)	116.1 (3)
O(1)—C(13)—C(14)	113.1 (4)	C(5)—C(6)—C(7)	108.5 (4)
O(2)—C(9)—C(8a)	120.4 (3)	C(6)—C(5)—C(10a)	106.3 (3)
O(2)—C(9)—C(9a)	120.6 (3)	C(5)—C(10a)—C(8a)	102.7 (3)
O(3)—C(13)—C(14)	125.6 (4)	C(5)—C(10a)—C(10)	113.9 (3)
C(1)—C(2)—C(3)	106.4 (3)	C(6)—C(5)—C(12)	99.0 (4)
C(2)—C(1)—C(9a)	108.4 (3)	C(10a)—C(5)—C(12)	99.8 (3)
C(1)—C(9a)—C(4a)	102.0 (2)	C(5)—C(12)—C(8)	94.2 (3)
C(1)—C(9a)—C(9)	113.7 (3)	C(6)—C(7)—C(8)	107.5 (4)
C(2)—C(1)—C(11)	100.7 (3)	C(7)—C(8)—C(8a)	106.6 (3)
C(9a)—C(1)—C(11)	98.9 (3)	C(7)—C(8)—C(12)	100.5 (3)
C(1)—C(11)—C(4)	93.2 (3)	C(8)—C(8a)—C(9)	115.4 (3)
C(2)—C(3)—C(4)	108.3 (3)	C(8)—C(8a)—C(10a)	102.7 (3)
C(3)—C(4)—C(4a)	109.9 (3)	C(8a)—C(8)—C(12)	100.0 (3)
C(3)—C(4)—C(11)	100.3 (3)	C(8a)—C(9)—C(9a)	119.1 (3)
C(4)—C(4a)—C(9a)	102.6 (3)	C(9)—C(8a)—C(10a)	116.5 (3)
C(4)—C(4a)—C(10)	119.1 (3)	C(8a)—C(10a)—C(10)	112.9 (3)

C(1)—C(2)—C(3)—C(4)	−0.2 (5)	C(10a)—C(5)—C(6)—C(7)	70.5 (5)
C(2)—C(3)—C(4)—C(4a)	70.1 (5)	C(4a)—C(10)—C(10a)—C(8a)	−44.3 (4)
C(3)—C(4)—C(4a)—C(9a)	−64.4 (4)	C(10)—C(10a)—C(8a)—C(9)	3.2 (4)
C(4)—C(4a)—C(9a)—C(1)	−2.2 (3)	C(10a)—C(8a)—C(9)—C(9a)	35.3 (4)
C(4a)—C(9a)—C(1)—C(2)	68.5 (3)	C(8a)—C(9)—C(9a)—C(4a)	−32.5 (4)
C(9a)—C(1)—C(2)—C(3)	−69.5 (4)	C(9)—C(9a)—C(4a)—C(10)	−8.5 (4)
C(5)—C(6)—C(7)—C(8)	−0.6 (5)	C(9a)—C(4a)—C(10)—C(10a)	47.3 (4)
C(6)—C(7)—C(8)—C(8a)	−70.1 (4)	C(4a)—C(10)—O(1)—C(13)	98.2 (4)
C(7)—C(8)—C(8a)—C(10a)	68.1 (4)	C(10a)—C(10)—O(1)—C(13)	−136.4 (4)
C(8)—C(8a)—C(10a)—C(5)	−0.9 (3)	C(10)—O(1)—C(13)—O(3)	10.3 (7)
C(8a)—C(10a)—C(5)—C(6)	−65.1 (4)	C(10)—O(1)—C(13)—C(14)	−169.1 (4)

Compound (*B*)

O(1)—C(1a)	1.441 (2)	C(3a)—C(4)	1.601 (2)
O(1)—C(8a)	1.464 (2)	C(3a)—C(6a)	1.543 (2)
O(2)—C(3)	1.498 (2)	C(4)—C(4a)	1.551 (3)
O(2)—C(11)	1.315 (2)	C(4)—C(10)	1.522 (2)
O(3)—C(11)	1.184 (1)	C(4a)—C(5a)	1.467 (2)
O(4)—C(7)	1.447 (2)	C(5a)—C(6)	1.562 (2)
O(5)—C(4a)	1.491 (2)	C(6)—C(6a)	1.584 (2)
O(5)—C(5a)	1.474 (2)	C(6)—C(10)	1.540 (3)
C(1a)—C(2)	1.562 (2)	C(6a)—C(7)	1.517 (3)
C(1a)—C(8a)	1.479 (2)	C(7)—C(7a)	1.532 (3)
C(2)—C(2a)	1.581 (2)	C(7a)—C(8)	1.570 (2)
C(2)—C(9)	1.556 (3)	C(8)—C(8a)	1.573 (2)
C(2a)—C(3)	1.500 (3)	C(8)—C(9)	1.572 (2)
C(2a)—C(7a)	1.568 (2)	C(11)—C(12)	1.478 (2)
C(3)—C(3a)	1.495 (3)		

O(1)—C(1a)—C(2)	119.6 (1)	O(5)—C(5a)—C(4a)	60.9 (1)
O(1)—C(1a)—C(8a)	60.2 (1)	O(5)—C(5a)—C(6)	123.6 (1)
C(1a)—O(1)—C(8a)	61.2 (1)	C(1a)—C(2)—C(2a)	106.3 (1)
O(1)—C(8a)—C(1a)	58.6 (1)	C(1a)—C(2)—C(9)	99.6 (1)
O(1)—C(8a)—C(8)	106.5 (1)	C(2)—C(1a)—C(8a)	108.7 (1)
O(2)—C(3)—C(2a)	105.6 (1)	C(1a)—C(8a)—C(8)	101.3 (1)
O(2)—C(3)—C(3a)	106.0 (1)	C(2)—C(2a)—C(3)	114.3 (1)
C(3)—O(2)—C(11)	119.3 (1)	C(2)—C(2a)—C(7a)	103.2 (1)
O(2)—C(11)—O(3)	124.1 (1)	C(2a)—C(2)—C(9)	99.3 (1)
O(2)—C(11)—C(12)	109.4 (1)	C(2)—C(9)—C(8)	95.2 (1)
O(3)—C(11)—C(12)	126.4 (1)	C(2a)—C(3)—C(3a)	118.4 (1)
O(4)—C(7)—C(6a)	107.4 (1)	C(3)—C(2a)—C(7a)	111.6 (1)
O(4)—C(7)—C(7a)	108.1 (1)	C(2a)—C(7a)—C(7)	116.7 (1)
O(5)—C(4a)—C(4)	108.4 (1)	C(2a)—C(7a)—C(8)	104.1 (1)
O(5)—C(4a)—C(5a)	59.8 (1)	C(3)—C(3a)—C(4)	119.8 (1)
C(4a)—O(5)—C(5a)	59.3 (1)	C(3)—C(3a)—C(6a)	113.1 (1)
C(3a)—C(4)—C(4a)	106.3 (1)	C(5a)—C(6)—C(6a)	108.4 (1)
C(3a)—C(4)—C(10)	101.9 (1)	C(5a)—C(6)—C(10)	94.4 (1)
C(4)—C(3a)—C(6a)	101.3 (1)	C(6)—C(6a)—C(7)	111.5 (1)

Table 4 (*cont.*)

C(3a)—C(6a)—C(6)	104.4 (1)	C(6a)—C(6)—C(10)	101.2 (1)
C(3a)—C(6a)—C(7)	116.4 (1)	C(6a)—C(7)—C(7a)	117.0 (1)
C(4)—C(4a)—C(5a)	98.0 (1)	C(7)—C(7a)—C(8)	113.8 (1)
C(4a)—C(4)—C(10)	106.0 (1)	C(7a)—C(8)—C(8a)	100.9 (1)
C(4)—C(10)—C(6)	94.8 (1)	C(7a)—C(8)—C(9)	99.0 (1)
C(4a)—C(5a)—C(6)	110.7 (1)	C(8a)—C(8)—C(9)	106.4 (1)

C(2)—C(1a)—C(8a)—C(8)	−11.4 (2)	C(3a)—C(4)—C(4a)—C(5a)	−81.1 (1)
C(1a)—C(8a)—C(8)—C(7a)	80.4 (1)	C(4)—C(4a)—C(5a)—C(6)	11.1 (2)
C(8a)—C(8)—C(7a)—C(2a)	−73.0 (1)	C(4a)—C(5a)—C(6)—C(6a)	59.8 (2)
C(8)—C(7a)—C(2a)—C(2)	0.1 (2)	C(5a)—C(6)—C(6a)—C(3a)	−65.2 (2)
C(7a)—C(2a)—C(2)—C(1a)	66.6 (1)	C(6)—C(6a)—C(3a)—C(4)	1.8 (2)
C(2a)—C(2)—C(1a)—C(8a)	−61.5 (2)	C(6a)—C(3a)—C(4)—C(4a)	73.8 (1)
C(2a)—C(3)—C(3a)—C(6a)	−49.4 (2)	C(2a)—C(3)—O(2)—C(11)	135.2 (1)
C(3)—C(3a)—C(6a)—C(7a)	7.9 (2)	C(3a)—C(3)—O(2)—C(11)	−98.3 (1)
C(3a)—C(6a)—C(7)—C(7a)	32.3 (2)	C(3)—O(2)—C(11)—O(3)	−7.8 (2)
C(6a)—C(7)—C(7a)—C(2a)	−34.8 (2)	O(4)—C(7)—C(7a)—C(8)	82.6 (2)
C(7)—C(7a)—C(2a)—C(3)	−3.1 (2)	O(4)—C(7)—C(6a)—C(6)	34.2 (2)
C(7a)—C(2a)—C(3)—C(3a)	46.2 (2)		

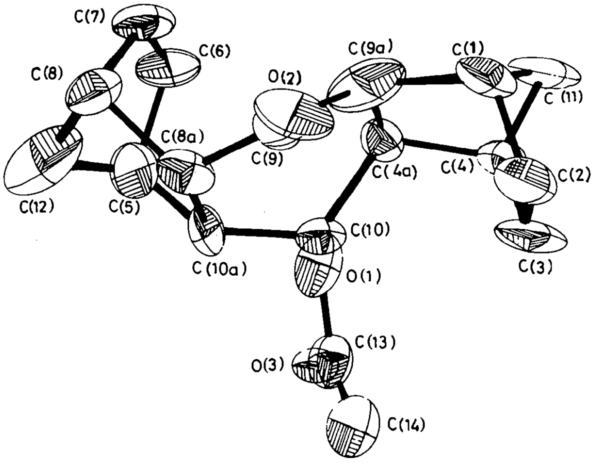


Fig. 1. *ORTEP* plot of a molecule of compound (*A*) with the thermal ellipsoids drawn at the 50% probability level showing the atom-labelling scheme.

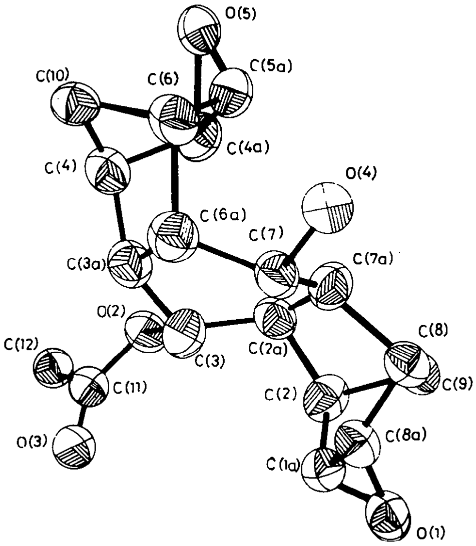


Fig. 2. *ORTEP* plot of a molecule of compound (*B*) with the thermal ellipsoids drawn at the 50% probability level showing the atom-labelling scheme.

The authors are grateful to Dr P. Engel, Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Switzerland, for providing the unpublished results of his studies. Thanks are due to the Head of the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, for the use of the CAD-4 diffractometer, and to Dr D. V. Ramana, Chemistry Department, IIT, Madras, for useful discussions. The authors are grateful to the referees for their comments and suggestions.

References

BAKTHAVATCHALAM, R. (1987). PhD thesis, Indian Institute of Technology, Madras.

BROWN, R., BRUCE, J. M., HUDSON, D. W. & MILLS, O. S. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 132–135.

DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structures*, Vol. I. New York: Plenum Press.

ENGEL, P. (1988). Personal communication.

GANESH, V., VARGHESE, B., SESHASAYEE, M., BAKTHAVATCHALAM, R. & RAMADAS, S. R. (1989). *Acta Cryst.* C**45**, 1551–1553.

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

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

ROBBINS, R. F. (1970). *Polymers in Space Research*, edited by C. L. SEGAL, M. SHEN & F. H. KELLEY, pp. 331–344. New York: Marcell Dekker.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

WATSON, W. H., NAGL, A., KASHYAP, R., MARCHAND, A. P. & VIDYASAGAR, V. (1990). *Acta Cryst.* C**46**, 1265–1268.

Acta Cryst. (1993). C**49**, 307–310

The Absolute Configuration of (+)-2-Benzyl-2-[*N*-(*α*-phenylethyl)amino]cyclohexanone Hydrochloride

BY ROLF PLATZBECKER AND GEORG WILL

Mineralogisches Institut, Universität Bonn, Poppelsdorfer Schloss, D-5300 Bonn 1, Germany

KURT HÜMMER* AND EDGAR WECKERT*

Institut für Angewandte Physik, Lehrstuhl für Kristallographie, Bismarckstrasse 10, D-8520 Erlangen, Germany

AND GERHARD LAUKTIEN† AND AUGUST W. FRAHM‡

Institut für Pharmazeutische Chemie, Universität Bonn, Kreuzbergweg 26, D-5300 Bonn 1, Germany

(*Received* 19 *July* 1991; *accepted* 20 *August* 1992)

Abstract. $C_{21}H_{25}NO.HCl$, $M_r = 343.90$, orthorhombic, $P2_12_12_1$, $a = 8.588\,(1)$, $b = 11.700\,(1)$, $c = 18.130\,(2)$ Å, $V = 1821.7\,(4)$ Å^3, $Z = 4$, $D_x = 1.254$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.139$ mm^{-1}, $F(000) = 736$, $T = 293$ K, final $R = 0.037$ for 3192 observed reflections. Condensation of 2-(benzyloxy)cyclohexanone with (*R*)-1-phenylethylamine yields, by rearrangement, an unexpected reaction product mixture of (*αR*,2*S*)- and (*αR*,2*R*)-2-benzyl-2-[*N*-(*α*-phenylethyl)amino]cyclohexanone hydrochlorides. The absolute configuration of one of the epimers, (+)-2-benzyl-2-[*N*-(*α*-phenylethyl)amino]cyclohexanone hydrochloride, is elucidated as (*αR*,2*S*) by X-ray structure analysis, showing the cyclohexanone ring in the chair conformation with the benzyl group in an axial and the *α*-phenylethylamino group in an equatorial position. N—H(Cl) hydrogen bonds are found along [100].

Introduction. An efficient synthesis of optically active *cis*-2-alkoxy and 2-aryloxycyclohexanamines has been reported (Lauktien & Frahm, 1990). The unexpected title compound, (+)-2-benzyl-2-[*N*-(*α*-phenylethyl)amino]cyclohexanone hydrochloride (3), was isolated after condensation and rearrangement

---

* Present address: Institut für Kristallographie, Universität Karlsruhe (TH), Engesserstrasse, Geb. 30.45, D-7500 Karlsruhe, Germany.

† Present address: Chemisches Landesuntersuchungsamt, Sperlichstrasse 19, D-4400 Münster, Germany.

‡ To whom correspondence should be addressed at Pharmazeutisches Institut, Universität Freiburg, Hermann-Herder-Strasse 9, D-7800 Freiburg, Germany.

0108-2701/93/020307-04$06.00 © 1993 International Union of Crystallography