Acta Cryst. (1980). **B36**, 2104–2108

On the Conformation of a Tricyclic Crown Ether, $C_{56}H_{68}O_{10}$*

By Israel Goldberg

Institute of Chemistry, Tel-Aviv University, Tel Aviv, Israel

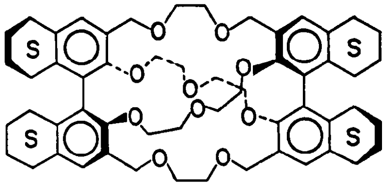
(*Received* 30 *January* 1980; *accepted* 16 *April* 1980)

Abstract

$C_{56}H_{68}O_{10}$ is orthorhombic, $P2_12_12_1$, at 113 K with a = 8·890 (1), b = 20·230 (3), c = 25·693 (5) Å, V = 4620·8 Å^3, Z = 4, D_c = 1·295 Mg m^{-3}. Final R = 0·057 for 2920 reflections. The four-stranded decaether molecule has approximate C_2 symmetry. In the observed conformation intramolecular cavities are filled by inward-turning methylene groups, some of the O—C—C—O conformational units being characterized by an unusual pattern of torsion angles.

Introduction

The title compound constitutes part of our investigation into the structural chemistry of crown ethers. It is the first example of a tricyclic system, consisting of two 1,1′-ditetralyl units bridged by four polyether strands at their 2 and 3 positions (formula shown).



In molecular models, the ten nucleophilic O atoms can form either a spherical or a cylindrical cavity suitable for inclusion of one or two metal cations of appropriate size; the resulting model structures resemble those observed for the three-dimensional metal-inclusion complexes of cryptands (Lehn & Montavon, 1978, and references therein). The synthesis and binding characteristics of this ligand have been reported (Helgeson, Tarnowski & Cram, 1979); for example, in a chloroform solution it exhibits a significantly higher binding ability for K^+ than for NH_4^+. Although attempts to form crystalline complex salts have thus far failed, it seemed important to elucidate the preferred conformation of the free host molecule in the solid.

Single crystals of the (S,S) isomer were kindly supplied by Professor Cram of the University of California at Los Angeles. The diffraction experiment was carried out at 113 ± 5 K, and there is no apparent phase transition between room temperature and 113 K. The low temperature was maintained by a low-temperature apparatus designed by Strouse (1976). The unit-cell dimensions were determined from 2θ measurements of 15 centered reflections, and refined by least squares. Intensities were collected in the ω–2θ mode on a four-circle diffractometer (Syntex $P\bar{1}$) with graphite-monochromatized Cu $K\alpha$ radiation (λ_{mean} = 1·5418 Å). 4669 unique reflections were recorded out to 2θ = 150° with a constant scan speed of 2° min^{-1}, scan range from 1·0° below $K\alpha_1$ to 1·0° above $K\alpha_2$, and stationary background measurements at both ends of each scan. Data were corrected for Lorentz and polarization effects, but not for absorption or secondary extinction. Final calculations were based on 2920 observations above threshold, $F_o^2 \geq 3\sigma(F_o^2)$. The structure was solved by a combination of direct methods (*MULTAN* 74; Main, Woolfson, Lessinger, Germain & Declercq, 1974) and Fourier techniques. A successful determination of phases emerged when the tangent-formula refinement in space group $P2_12_12_1$ was applied to 448 reflections with $|E| \geq$ 1·60 and 4000 triple-phase relationships. Only 64 of the 66 non-hydrogen atoms of the structure were located in a subsequent E map; the remaining two atoms were found on difference maps. A similar phase-determination procedure based on an *identical* starting set of seven reflections, but containing an additional 51 structure factors with 1·55 $\leq E <$ 1·60, failed to produce even a partially correct representation of the structure. Apparently, this is due to missing as well as possibly false links in the limited list of 4000 Σ_2 relationships formed from the increased set of structure factors (Lessinger, 1976).

Anisotropic refinement of the heavy-atom structure proceeded by block-diagonal least squares, the molecule being divided into two blocks. All the H atoms were introduced in calculated positions with

---

* A preliminary account of this work has been presented at the Third European Crystallographic Meeting, Zurich, 6th September, 1976. The systematic name for the compound is: (S,S)-20,23,26,-47,50,53,56,59,62,65-decaoxaundecacyclo[26.26.6.6^{18,45}.0^{3,8}.0^{9,54}.-0^{10,19}.0^{11,16}.0^{27,36}.0^{30,35}.0^{37,46}.0^{38,43}]hexahexaconta-1(54),2,8,-10(19),11(16),17,27(36),28,30(35),37(46),38(43),44-dodecaene.

0567-7408/80/092104-05\$01.00

Table 1. *Fractional coordinates of the non-hydrogen atoms*

E.s.d.'s are given in parentheses in units of the last decimal place.

	x	*y*	*z*
C(1)	.5905(8)	.1333(3)	.4510(3)
C(2)	.5984(8)	.1292(3)	.3973(3)
C(3)	.5298(8)	.1777(3)	.3656(3)
C(4)	.5450(9)	.1746(3)	.3076(3)
C(5)	.5085(10)	.2400(4)	.2807(3)
C(6)	.3616(11)	.2689(4)	.3018(3)
C(7)	.3721(9)	.2628(3)	.3586(3)
C(8)	.4480(8)	.2287(3)	.3980(3)
C(9)	.4394(9)	.2293(3)	.4428(3)
C(10)	.5126(9)	.1846(3)	.4755(3)
C(11)	.5017(10)	.1938(4)	.5331(3)
O(12)	.3601(7)	.2137(2)	.5503(2)
C(13)	.2572(10)	.1619(4)	.5504(4)
C(14)	.2581(10)	.1272(4)	.6026(4)
O(15)	.3933(6)	.0884(3)	.6062(2)
C(16)	.4143(9)	.0603(3)	.6563(3)
C(17)	.5555(9)	.0200(3)	.6555(2)
C(18)	.6856(9)	.0429(3)	.6774(3)
C(19)	.8179(8)	.0054(3)	.6787(2)
C(20)	.9583(9)	.0340(3)	.7032(3)
C(21)	1.0604(9)	-.0191(4)	.7249(3)
C(22)	1.0917(9)	-.0706(4)	.6832(3)
C(23)	.9498(9)	-.1035(3)	.6632(3)
C(24)	.8142(8)	-.0594(3)	.6589(2)
C(25)	.6841(8)	-.0832(3)	.6362(2)
C(26)	.5562(8)	-.0441(3)	.6338(2)
O(27)	.4238(5)	-.0679(2)	.6120(2)
C(28)	.4223(9)	-.0674(4)	.5557(3)
C(29)	.2656(9)	-.0544(3)	.5380(3)
O(30)	.2469(6)	-.0716(2)	.4855(2)
C(31)	.2829(10)	-.0226(4)	.4480(3)
C(32)	.4417(8)	-.0312(3)	.4294(3)
O(33)	.4547(5)	.0073(2)	.3818(2)
C(34)	.6022(8)	.0122(3)	.3656(3)
C(35)	.6784(8)	.0718(3)	.3724(2)
C(36)	.8299(8)	.0792(3)	.3564(2)
C(37)	.9129(8)	.1426(3)	.3660(3)
C(38)	1.0830(9)	.1312(4)	.3682(3)
C(39)	1.1328(9)	.0964(4)	.3180(3)
C(40)	1.0620(9)	.0291(4)	.3126(3)
C(41)	.8991(8)	.0263(3)	.3310(2)
C(42)	.8205(9)	-.0320(3)	.3230(3)
C(43)	.6743(9)	-.0406(3)	.3405(2)
C(44)	.6016(9)	-.1079(3)	.3339(3)
O(45)	.6665(6)	-.1491(2)	.3731(2)
C(46)	.6091(9)	-.2151(3)	.3708(3)
C(47)	.7022(9)	-.2551(3)	.4082(3)
O(48)	.6714(6)	-.2350(2)	.4592(2)
C(49)	.7831(9)	-.2561(3)	.4958(3)
C(50)	.7364(8)	-.2337(3)	.5485(2)
C(51)	.6861(8)	-.2820(3)	.5823(3)
C(52)	.6347(9)	-.2698(3)	.6322(3)
C(53)	.5847(10)	-.3274(3)	.6664(3)
C(54)	.4862(11)	-.3058(3)	.7124(3)
C(55)	.5552(11)	-.2456(4)	.7394(3)
C(56)	.5705(9)	-.1869(3)	.7032(3)
C(57)	.6293(8)	-.2040(3)	.6496(2)
C(58)	.6796(8)	-.1534(3)	.6162(3)
C(59)	.7327(8)	-.1681(3)	.5665(3)
O(60)	.7683(7)	-.1129(2)	.5379(2)
C(61)	.8620(9)	-.1121(3)	.4949(3)
C(62)	.8752(8)	-.0430(3)	.4742(3)
O(63)	.9486(6)	.0015(2)	.5092(2)
C(64)	.8528(9)	.0437(3)	.5376(3)
C(65)	.7903(9)	.1004(3)	.5073(3)
O(66)	.6555(5)	.0836(2)	.4801(2)

C–H = 1·04 Å. No attempt was made to refine the positions or isotropic thermal parameters ($U = 0{\cdot}05$ Å^2) of the H atoms. The function minimized was $\sum w(\Delta F)^2$, where $w = 1/\sigma^2(F_o)$. During the refinement of a total of 595 structural parameters it became apparent that two of the peripheral bonds, C(5)–C(6) and C(54)–C(55), are disordered to a minor extent. Thus, in order to avoid unreliable distortions of the molecular geometry by artificial effects of thermal motion, the corresponding C(sp^3)–C(sp^3) bond lengths were constrained to 1·53 Å; in a preliminary unconstrained refinement the C(5)–C(6) and C(54)–C(55) distances converged at 1·46 and 1·43 Å, respectively. Similarly, the refined values of 1·46 Å for C(31)–C(32) and 1·48 Å for C(61)–C(62) were adjusted to and fixed at 1·50 Å, the normal length of a C(sp^3)–C(sp^3) bond in crown ether rings. The refinement was terminated with $R = 0{\cdot}057$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2} = 0{\cdot}063$. The final goodness-of-fit parameter is 1·53. In the difference map calculated after the last cycle there were no peaks >0·4 e Å^{-3}. Coordinates of the non-hydrogen atoms are given in Table 1.*

In order to assess the extent of the postulated disorder in two of the six-membered saturated rings a disordered model of the molecular structure was constructed, assuming that each of the CH_2(5)–CH_2(6) and CH_2(54)–CH_2(55) ethylenic groups is independently disordered between two different sites. Subsequent constrained least-squares calculations included refinement of relative occupancy factors, orientational and positional parameters of the assumedly rigid CH_2–CH_2 groups and individual thermal parameters of the atoms. At convergence $R = 0{\cdot}055$ and $R_w = 0{\cdot}061$ for 609 refined parameters and 2920 observations. The results suggest that the atomic sites C(5), C(6) and C(54), C(55) given in Table 1 have approximate occupancies of only 0·85 and 0·65, respectively. The less probable sites of these atoms correspond to inverted conformations of the relevant peripheral rings with respect to the adjacent planar aryl groups. In all calculations, scattering factors for C and O were taken from Hanson, Herman, Lea & Skillman (1964), those for H from Stewart, Davidson & Simpson (1965).

Discussion

The geometry of the four-stranded tricyclic ligand is displayed in Fig. 1 with bond distances and angles listed in Tables 2 and 3. The covalent bonding parameters found in this structure are in agreement with those reported for related compounds (Goldberg, 1980). To some extent, a similar correlation applies to the conformational parameters as well [in this context it is important to keep in mind that the energetically preferred conformations about C–C and C–O bonds

---

* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35209 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in crown ethers are *gauche* (*g*) and *anti* (*a*), respectively}. Although the structural formula of the (*S*,*S*) isomer suggests D_2 symmetry (see above), the uncomplexed host is significantly folded in the crystal, possessing only approximate C_2 symmetry. In order to optimize intramolecular interactions within the ligand, the polyether bridges strung between the two nearly rigid 1,1′-ditetralyl units have different conformations (Fig. 1). It appears that the geometry of the O(27)–$(CH_2)_2O(CH_2)_2$–O(33) strand with aag^-g^+aa arrangements about the respective bonds is rather unusual, as, according to Dale (1980), such conformational units have not been found in structures of unsubstituted macrocyclic oligoethers. Since the torsion angles about C–C bonds in this group are *anti* rather than *gauche*, the CH_2(28) and CH_2(32) methylenes turn toward the center of the molecule and form van der Waals contacts with the O(60)–$(CH_2)_2O(CH_2)_2$–O(66) unit located on the opposite side of the cavity. The latter also has a distorted conformation (roughly $ag^+g^-g^-g^+a$), being displaced in a symmetrical manner from the rigid aryl rings (*b*) and (*c*) [Fig. 1(*a*)]. Relevant intramolecular distances include: C(24)···C(64) 3·77 (1), C(28)···C(64) 4·46 (1), C(32)···C(62) 4·03 (2), and C(34)···C(62) 3·86 (2) Å. The conformational data in Fig. 1(*b*) indicate that the cavities within the present ligand defined by various O···O distances [*e.g.*, O(15)···O(30) 4·67 (2), O(30)···O(45) 4·97 (1), O(15)···O(63) 5·80 (2), O(45)···O(63) 5·27 (1) and O(30)···O(63) 6·44 (2) Å] are filled with inward-turning CH_2 groups. Similar observations on related uncomplexed crown compounds have been reported (Dunitz & Seiler, 1974; Goldberg, 1978).

Table 2. *Bond distances* (Å)

C(1) - C(2)	1.384(10)	O(33) - C(34)	1.379(8)
C(1) - C(10)	1.398(10)	C(34) - C(35)	1.393(9)
C(2) - C(35)	1.504(9)	C(34) - C(43)	1.403(9)
C(2) - C(3)	1.412(9)	C(35) - C(36)	1.416(10)
C(3) - C(4)	1.498(9)	C(36) - C(37)	1.500(9)
C(3) - C(8)	1.411(9)	C(36) - C(41)	1.395(9)
C(4) - C(5)	1.526(10)	C(37) - C(38)	1.531(11)
C(5) - C(6)	1.530	C(38) - C(39)	1.532(11)
C(6) - C(7)	1.491(11)	C(39) - C(40)	1.506(11)
C(7) - C(8)	1.519(10)	C(40) - C(41)	1.524(11)
C(8) - C(9)	1.358(10)	C(41) - C(42)	1.388(10)
C(9) - C(10)	1.396(10)	C(42) - C(43)	1.386(11)
C(10) - C(11)	1.496(10)	C(43) - C(44)	1.517(9)
C(11) - O(12)	1.393(10)	C(44) - O(45)	1.428(8)
O(12) - C(13)	1.391(10)	O(45) - C(46)	1.431(8)
C(13) - C(14)	1.513(11)	C(46) - C(47)	1.505(10)
C(14) - O(15)	1.437(10)	C(47) - O(48)	1.399(8)
O(15) - C(16)	1.421(9)	O(48) - C(49)	1.433(9)
C(16) - C(17)	1.497(11)	C(49) - C(50)	1.489(10)
C(17) - C(18)	1.367(11)	C(50) - C(51)	1.382(9)
C(17) - C(26)	1.412(9)	C(50) - C(59)	1.405(9)
C(18) - C(19)	1.400(10)	C(51) - C(52)	1.383(10)
C(19) - C(20)	1.513(10)	C(52) - C(53)	1.525(10)
C(19) - C(24)	1.406(9)	C(52) - C(57)	1.405(9)
C(20) - C(21)	1.512(10)	C(53) - C(54)	1.536(11)
C(21) - C(22)	1.521(10)	C(54) - C(55)	1.530
C(22) - C(23)	1.515(11)	C(55) - C(56)	1.516(10)
C(23) - C(24)	1.504(10)	C(56) - C(57)	1.514(9)
C(24) - C(25)	1.382(10)	C(57) - C(58)	1.408(9)
C(25) - C(26)	1.386(10)	C(58) - C(59)	1.393(9)
C(25) - C(58)	1.512(8)	C(59) - O(60)	1.374(8)
C(26) - O(27)	1.388(9)	O(60) - C(61)	1.383(9)
O(27) - C(28)	1.447(9)	C(61) - C(62)	1.500
C(28) - C(29)	1.489(11)	C(62) - O(63)	1.430(8)
C(29) - O(30)	1.403(8)	O(63) - C(64)	1.409(9)
O(30) - C(31)	1.418(9)	C(64) - C(65)	1.494(10)
C(31) - C(32)	1.500	C(65) - O(66)	1.429(9)
C(32) - O(33)	1.456(8)	O(66) - C(1)	1.388(8)

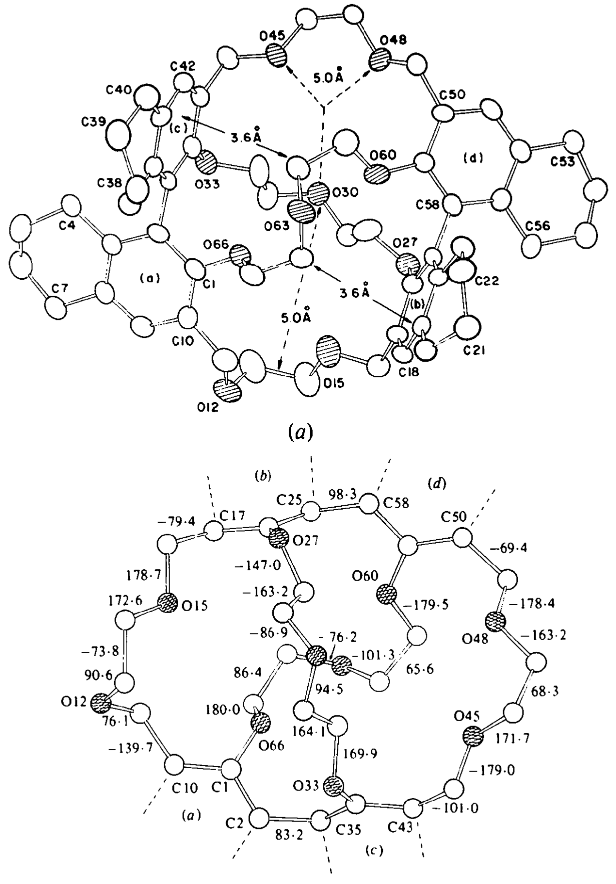


Fig. 1. (*a*) A perspective drawing of the molecular structure showing the numbering scheme. Thermal ellipsoids correspond to 50% probability. Average distances between various parts of the ligand are marked. (*b*) Torsion angles (°) along the four polyether strands. E.s.d.'s of all the angles range from 0·5 to 0·8° with an average of 0·7°.

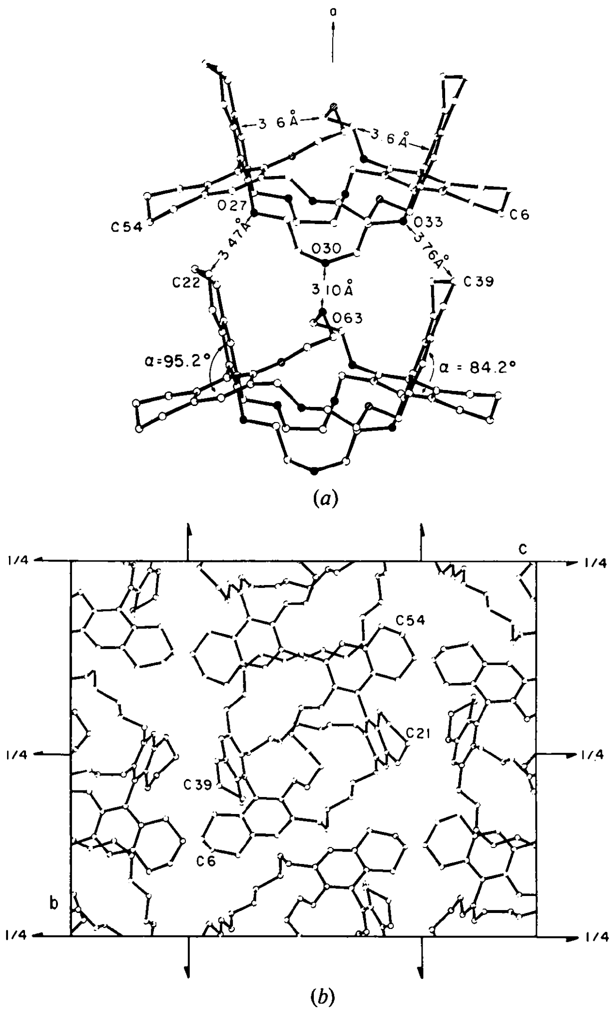
In the observed conformation the aryl groups on both sides of the molecule are nearly perpendicular to each other; the angles between their respective planes are near 84 and 95° (Fig. 2). The partially saturated outer rings in the 1,1′-ditetralyl units are nonplanar, some of the peripheral atoms deviating by as much as 0·6 Å from the planes of adjacent aromatic groups. Association of this ligand with metal and ammonium guest species is relatively poor (Helgeson, Tarnowski & Cram, 1979). Apparently, this is in part because four of the potential oxygen-ligating sites are attached to electron-withdrawing aryl substituents, and a relatively

Table 3. *Bond angles* (°)

C(10)-C(1) -C(2)	121.3(6)	O(33)-C(34)-C(43)	121.1(6)
C(10)-C(1) -O(66)	120.3(6)	C(43)-C(34)-C(35)	119.6(6)
O(66)-C(1) -C(2)	118.4(6)	O(33)-C(34)-C(35)	119.2(6)
C(1) -C(2) -C(35)	119.5(6)	C(34)-C(35)-C(2)	119.4(6)
C(1) -C(2) -C(3)	120.8(6)	C(34)-C(35)-C(36)	121.1(6)
C(3) -C(2) -C(35)	119.7(6)	C(36)-C(35)-C(2)	119.5(6)
C(2) -C(3) -C(8)	118.3(6)	C(35)-C(36)-C(41)	118.3(6)
C(8) -C(3) -C(4)	121.3(6)	C(41)-C(36)-C(37)	121.0(6)
C(2) -C(3) -C(4)	120.4(6)	C(35)-C(36)-C(37)	120.7(6)
C(3) -C(4) -C(5)	113.3(6)	C(36)-C(37)-C(38)	111.2(6)
C(4) -C(5) -C(6)	110.7(6)	C(37)-C(38)-C(39)	108.9(6)
C(5) -C(6) -C(7)	111.4(7)	C(38)-C(39)-C(40)	111.8(6)
C(6) -C(7) -C(8)	114.3(6)	C(39)-C(40)-C(41)	113.7(6)
C(7) -C(8) -C(3)	121.4(6)	C(40)-C(41)-C(36)	122.4(6)
C(3) -C(8) -C(9)	118.7(6)	C(36)-C(41)-C(42)	120.0(7)
C(7) -C(8) -C(9)	119.9(6)	C(40)-C(41)-C(42)	117.6(6)
C(8) -C(9) -C(10)	124.7(7)	C(41)-C(42)-C(43)	122.0(6)
C(9) -C(10)-C(1)	116.1(6)	C(42)-C(43)-C(34)	118.9(6)
C(1) -C(10)-C(11)	124.9(6)	C(34)-C(43)-C(44)	122.7(7)
C(9) -C(10)-C(11)	119.0(6)	C(42)-C(43)-C(44)	118.4(6)
C(10)-C(11)-O(12)	114.1(7)	C(43)-C(44)-O(45)	105.9(6)
C(11)-O(12)-C(13)	112.2(6)	C(44)-O(45)-C(46)	111.8(5)
O(12)-C(13)-C(14)	110.4(7)	O(45)-C(46)-C(47)	106.2(6)
C(13)-C(14)-O(15)	108.4(7)	C(46)-C(47)-O(48)	109.5(6)
C(14)-O(15)-C(16)	112.8(6)	C(47)-O(48)-C(49)	113.1(5)
O(15)-C(16)-C(17)	108.4(6)	O(48)-C(49)-C(50)	108.3(6)
C(16)-C(17)-C(26)	120.7(7)	C(49)-C(50)-C(59)	126.4(6)
C(16)-C(17)-C(18)	121.2(6)	C(49)-C(50)-C(51)	116.5(6)
C(26)-C(17)-C(18)	118.0(7)	C(59)-C(50)-C(51)	117.1(6)
C(17)-C(18)-C(19)	122.5(6)	C(50)-C(51)-C(52)	124.2(6)
C(18)-C(19)-C(24)	118.4(6)	C(51)-C(52)-C(57)	118.4(6)
C(18)-C(19)-C(20)	119.8(6)	C(51)-C(52)-C(53)	119.6(6)
C(24)-C(19)-C(20)	121.7(6)	C(57)-C(52)-C(53)	122.0(6)
C(19)-C(20)-C(21)	112.1(5)	C(52)-C(53)-C(54)	113.2(6)
C(20)-C(21)-C(22)	109.7(6)	C(53)-C(54)-C(55)	110.3(7)
C(21)-C(22)-C(23)	112.8(6)	C(54)-C(55)-C(56)	112.5(6)
C(22)-C(23)-C(24)	115.6(6)	C(55)-C(56)-C(57)	114.2(6)
C(23)-C(24)-C(25)	119.7(6)	C(56)-C(57)-C(58)	119.9(6)
C(23)-C(24)-C(19)	120.5(6)	C(56)-C(57)-C(52)	121.2(6)
C(19)-C(24)-C(25)	119.8(6)	C(52)-C(57)-C(58)	118.9(6)
C(24)-C(25)-C(26)	120.5(6)	C(57)-C(58)-C(59)	120.8(6)
C(24)-C(25)-C(58)	119.6(6)	C(57)-C(58)-C(25)	118.9(6)
C(58)-C(25)-C(26)	119.9(6)	C(59)-C(58)-C(25)	120.2(6)
C(25)-C(26)-O(27)	121.1(6)	C(58)-C(59)-O(60)	113.3(5)
C(25)-C(26)-C(17)	120.6(7)	C(58)-C(59)-C(50)	120.6(6)
O(27)-C(26)-C(17)	118.2(6)	C(50)-C(59)-O(60)	126.0(6)
C(26)-O(27)-C(28)	114.1(5)	C(59)-O(60)-C(61)	125.1(5)
O(27)-C(28)-C(29)	108.4(6)	O(60)-C(61)-C(62)	109.9(6)
C(28)-C(29)-O(30)	111.2(6)	C(61)-C(62)-O(63)	113.6(6)
C(29)-O(30)-C(31)	117.0(5)	C(62)-O(63)-C(64)	115.6(5)
O(30)-C(31)-C(32)	110.3(6)	O(63)-C(64)-C(65)	114.8(6)
C(31)-C(32)-O(33)	106.3(6)	C(64)-C(65)-O(66)	112.6(6)
C(32)-O(33)-C(34)	111.6(5)	C(65)-O(66)-C(1)	116.3(5)

large number of conformational degrees of freedom could be involved in the formation of an inclusion complex.

The crystal structure illustrated in Fig. 2 can be described as composed of sheets of molecules perpendicular to **c**, and related to each other by the 2_1^b screw axes. Packing interactions between adjacent sheets are particularly weak, all relevant nonbonding distances exceeding 4·1 Å. Within each layer, the molecular arrangement is determined by normal van der Waals contacts. Stacking of molecules along the shortest dimension of the cell is rather efficient, as the convex polyether part of one moiety is in close contact with the concave side of its neighbor along the stack. Probable positional disorder of the peripheral atoms C(5), C(6), C(54) and C(55) even at 113 K, indicated by large components of their thermal parameters along **a**, is consistent with the overall packing arrangement in this structure.



(*a*)

(*b*)

Fig. 2. Illustrations of the crystal structure. (*a*) Stacking interactions between adjacent molecules along **a**. The intermolecular distances shown have e.s.d.'s of 0·02 Å. The angular values represent angles between least-squares planes of the aryl groups. (*b*) Contents of the unit cell viewed down **a**. Symbols of some of the symmetry elements are marked.

Part of this research was carried out at the laboratory of Professor K. N. Trueblood and supported through his courtesy by an NSF grant. The author thanks Professor Trueblood, and Professor D. J. Cram for providing the crystals. Financial support by the Israel Commission for Basic Research is also acknowledged.

References

Dale, J. (1980). *Isr. J. Chem.* **20**. In the press.

Dunitz, J. D. & Seiler, P. (1974). *Acta Cryst.* B**30**, 2739–2741.

Goldberg, I. (1978). *Acta Cryst.* B**34**, 3387–3390.

Goldberg, I. (1980). *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogs*, Supplement E1, edited by S. Patai, pp. 175–214. London: John Wiley.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Helgeson, R. C., Tarnowski, T. L. & Cram, D. J. (1979). *J. Org. Chem.* **44**, 2538–2550.

Lehn, J. M. & Montavon, F. (1978). *Helv. Chim. Acta*, **61**, 67–82.

Lessinger, L. (1976). *Acta Cryst.* A**32**, 538–550.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

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

Strouse, C. E. (1976). *Rev. Sci. Instrum.* **47**, 871–876.

Acta Cryst. (1980). B**36**, 2108–2112

Structure de la Dihydro-10,11 5*H*-Dibenzo[*b*,*f*]azépine (Iminodibenzyle) Noyau Tricyclique des Antidépresseurs Imipraminiques

Par J. P. Reboul et B. Cristau

Laboratoire de Pharmacie Chimique, Faculté de Pharmacie, Université d'Aix-Marseille II, 27 *boulevard Jean-Moulin,* 13385 *Marseille CEDEX* 4, *France*

J. Estienne

Université des Sciences et de la Technologie d'Alger, Institut de Chimie, BP n° 9 *Dar El Beida, Alger, Algerie*

et J. P. Astier

Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Faculté des Sciences et Techniques de St Jérome, 13397 *Marseille CEDEX 4, France*

(*Reçu le* 7 *juin* 1979, *accepté le* 1 *avril* 1980)

Abstract

The structure of iminodibenzyl, $C_{14}H_{13}N$, parent molecule of a very important group of antidepressant drugs, has been determined from 2422 diffractometer data by direct methods and refined to a final residual R of 0·049. The space group is monoclinic, $P2_1/c$, with $a = 11{\cdot}604$ (4), $b = 11{\cdot}269$ (4), $c = 20{\cdot}050$ (8) Å; $\beta = 126{\cdot}55$ (4)°; $Z = 8$, $V = 2106{\cdot}2$ Å^3; $D_m = 1{\cdot}22$ (1), $D_x = 1{\cdot}23$ Mg m^{-3}. All the hydrogen atoms were placed by analyzing a section of the three-dimensional density function. The two independent molecules (I and II) have nearly the same fold configuration as phenothiazine: the dihedral angles between the two planes of the benzene rings are 151·3 (5) and 154·1 (3)° respectively for I and II.

Introduction

L'iminodibenzyle ou dihydro-10,11 5*H*-dibenzo[*b*,*f*]-azépine est un hétérocycle tricyclique azoté qui joue un rôle important en pharmacologie depuis la découverte de dérivés *N*-alkyl-aminés dotés de propriétés psychotropes qui en font de puissants médicaments antidépresseurs. Ces produits (Fig. 1), tels l'imipramine (Post, Kennard & Horn, 1975; Paulus, 1978) et la clomipramine (Post & Horn, 1977), ont été étudiés en radiocristallographie sous forme de sels.

En revanche la structure de l'hétérocycle de base, l'iminodibenzyle ne semble pas avoir retenu l'attention des cristallographes. Elle fait l'objet du présent mémoire et nous conduira ultérieurement à étudier à travers la paramétrisation des résultats expérimentaux, les variations conformationnelles subies par l'iminodibenzyle du fait des substituants, à la manière de recherches précédemment conduites en série phénothiazinique (Reboul & Cristau, 1977, 1978).

Données expérimentales

L'iminodibenzyle fourni par Fluka, Buchs SG, a été dissous dans l'éthanol absolu (10 g/50 ml) et porté à reflux pendant 1 h.

L'évaporation lente à 273 K (5 à 6 jours) a fourni des cristaux de forme pseudo-rhomboédrique.

Des clichés effectués sur chambre de précession avec la longueur d'onde du cuivre ($\lambda = 1{,}5418$ Å) ont permis de déterminer la maille cristalline qui a été affinée sur

0567-7408/80/092108-05$01.00