Crystal Structure and Absolute Configuration of α-(1-Phenylethylimino)benzyl Phenyl Ketone

By I. Fonseca, S. Martínez-Carrera and S. García-Blanco

Departamento de Rayos X, Instituto de Química-Física 'Rocasolano', Serrano 119, Madrid-6, Spain

Abstract

The structure of $C_{22}H_{19}NO$ has been solved by direct methods [space group $P2_12_12_1$, $a = 18.7542$ (9), $b = 10.2589$ (4), $c = 9.1836$ (3) Å] and refined to $R = 0.03$ and $R_w = 0.04$ for 1579 Bijvoet pairs. 75 enantiomer-sensitive Bijvoet pairs were employed to determine the absolute configuration. No effect of conjugation in the $O=C(7)-C(8)=N$ sequence was detected.

Introduction

García-Ruano & Pérez-Ossorio (1975) have prepared some benzyl derivatives of imines to determine their mutarotational behaviour. The title compound, which belongs to this group of compounds having an asymmetric C atom, was studied to establish the absolute configuration and to determine whether conjugation exists in the sequence $O=C(7)-C(8)=N$.

Experimental

Colourless crystals were kindly supplied by Professor R. P. Pérez-Ossorio of the Departamento de Química Orgánica de la Facultad de Ciencias Químicas de la Universidad Complutense de Madrid. These crystals are elongated along *b* and were recrystallized by evaporation of an ethanolic solution. Preliminary cell dimensions and space group were determined from Weissenberg and precession photographs. Accurate cell parameters were determined by least squares from the setting angles of 31 reflections measured on a

diffractometer with Cu $K\alpha$ radiation monochromatized by a graphite crystal. Crystal data are given in Table 1.

Intensities were measured from a crystal $0.43 \times 0.32 \times 0.14$ mm on a Philips PW 1100 four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation for $3 < \theta < 30°$. The ω–2θ scan technique was used. Two reflections were used as standards and remeasured after every 54 reflections; no decomposition was observed. Of the 3667 *hkl* and *h̄k̄l̄* reflections measured, 3084 were considered as observed with $I < 2\sigma(I)$, σ being determined from counting statistics. Lorentz and polarization corrections were applied, but no correction was made for absorption.

Structure determination

The structure was solved with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1974). The phases of 200 reflections were determined. In the *E* map calculated with these phases, 23 of the 24 non-hydrogen atoms were located. A structure factor calculation at this stage with all observed reflections and an overall isotropic temperature factor obtained from a Wilson plot gave $R = 0.468$. A Fourier synthesis gave the position of the remaining non-hydrogen atom. The structure was refined by full-matrix least squares. A single scale factor was used. Refinement with isotropic temperature factors gave $R = 0.114$ and reasonable temperature coefficients. Further refinement with anisotropic temperature factors and $w = 1.0$ reduced R to 0.082. At this stage a difference map located the H atoms, which were included with isotropic temperature factors. The process of refining non-hydrogen atoms anisotropically was stopped when the changes in all parameters became $<0.24\sigma$. In order to prevent bias in wF_o or $\sin\theta/\lambda$, the last steps of the refinement were performed with the weighting scheme $w = K/|f(F_o)|^2$, with $f(F_o) = 0.45 - 0.05|F_o|$ for $F_o \leq 4.0$, $f(F_o) = 0.19 + 0.02|F_o|$ for $F_o > 4.0$ and $K = 0.58$.

The absolute configuration, Fig. 1, was determined by refinement of both enantiomers with the moduli of

Table 1. *Crystal data*

$C_{22}H_{19}NO$			
M_r	313.27	V	1766.78 Å³
λ(Cu $K\alpha$)	1.5418 Å	Z	4
μ	0.569 mm⁻¹	D_c	1.178 Mg m⁻³
a	18.7542 (9) Å	$F(000)$	664
b	10.2589 (4)	Space group	$P2_12_12_1$
c	9.1836 (3)		

the 1579 Bijvoet pairs (Bijvoet, Peerdeman & van Bommel, 1951), giving $R = 0.03670$ and 0.03672 ($R_w = 0.04559$ and 0.04576, respectively). This was confirmed by comparing the 75 most relevant Bijvoet pairs giving the following discrepancy index calculated by *CONFAB* (Martínez-Ripoll & Fayos, 1977): average Bijvoet difference $R_1 = \sum ||F_o(+h) - F_o(-h)| - |F_c(+h) - F_c(-h)||/N = 0.148$ (0.199 for the enantiomorph) and average Bijvoet ratio $R_2 = \sum |R_o - R_c|/N = 0.034$ (0.042), with $R_o = |F_o(+h)^2 - F_o(-h)^2|/\langle F_o \rangle$, $R_c = |F_c(+h)^2 - F_c(-h)^2|/\langle F_c \rangle$, and N = number of Bijvoet pairs. Scattering factors for all atoms and anomalous-dispersion corrections, f' and f'' for O, N and C, were taken from *International Tables for X-ray Crystallography* (1974).

A final difference synthesis was essentially featureless with the highest peak and deepest trough equal to 0.10 and -0.15 e Å^{-3}, respectively.

Final atomic parameters are given in Tables 2 and 3.*

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34552 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
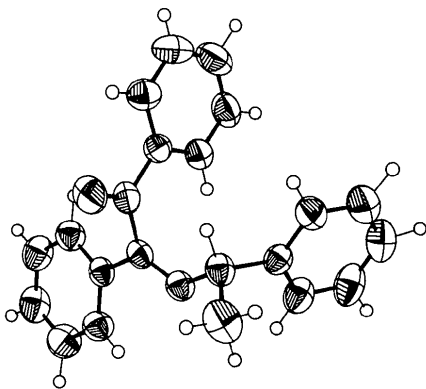

Fig. 1. Conformation of the molecule.

Discussion

The overall shape of the molecule is illustrated in Fig. 1. Bond lengths and angles are shown in Fig. 2 which also shows the atom numbering. Further details of the molecular geometry are recorded in Tables 4 and 5. No conjugation effects are found in the bonds C_{ph}–C(7)=O, C_{ph}–C(8)=N and N=C(8)–C(7)=O. This lack of conjugation is due to the rotation of phenyl rings A and C round the bonds C(1)–C(7) and C(8)–C(9) in the first two cases and to the deviation of the O atom from the plane C(7)–C(8)=N–C(15) in the third. Consequently C(7)–C(8) = 1.530 (2) Å is long.

Table 3. *Atomic coordinates* ($\times 10^3$) *and bond distances* (Å) *for the* H *atoms with e.s.d.'s in parentheses*

	x	y	z
H(2)	−288 (1)	−573 (2)	−482 (2)
H(3)	−209 (1)	−415 (2)	−376 (3)
H(4)	−247 (2)	−246 (3)	−229 (4)
H(5)	−372 (2)	−256 (4)	−175 (4)
H(6)	−450 (1)	−410 (2)	−278 (2)
H(10)	−434 (1)	−485 (2)	−673 (2)
H(11)	−462 (1)	−448 (2)	−944 (3)
H(12)	−470 (1)	−630 (2)	−85 (2)
H(13)	−440 (1)	−844 (2)	−18 (2)
H(14)	−409 (1)	−869 (2)	−763 (2)
H(15)	−374 (1)	−768 (2)	−290 (2)
H(17)	−242 (1)	−938 (2)	−513 (2)
H(18)	−112 (1)	−935 (3)	−459 (3)
H(19)	−69 (1)	−819 (3)	−239 (3)
H(20)	−153 (1)	−739 (3)	−70 (3)
H(21)	−281 (1)	−729 (2)	−139 (2)
H(221)	−366 (1)	−995 (3)	−227 (3)
H(222)	−431 (2)	−977 (3)	−335 (3)
H(223)	−353 (1)	−37 (2)	−411 (3)

C(2)–H(2)	0.93 (2)	C(15)–H(15)	1.07 (2)
C(3)–H(3)	0.94 (2)	C(17)–H(17)	0.99 (2)
C(4)–H(4)	1.10 (3)	C(18)–H(18)	1.01 (3)
C(5)–H(5)	0.88 (4)	C(19)–H(19)	1.10 (3)
C(6)–H(6)	0.91 (2)	C(20)–H(20)	1.11 (3)
C(10)–H(10)	1.04 (2)	C(21)–H(21)	1.06 (2)
C(11)–H(11)	1.01 (3)	C(22)–H(221)	1.01 (3)
C(12)–H(12)	0.90 (2)	C(22)–H(222)	0.95 (3)
C(13)–H(13)	1.06 (2)	C(22)–H(223)	1.12 (3)
C(14)–H(14)	0.95 (2)		

Table 2. *Final atomic parameters and their e.s.d.'s for non-hydrogen atoms* ($\times 10^4$)

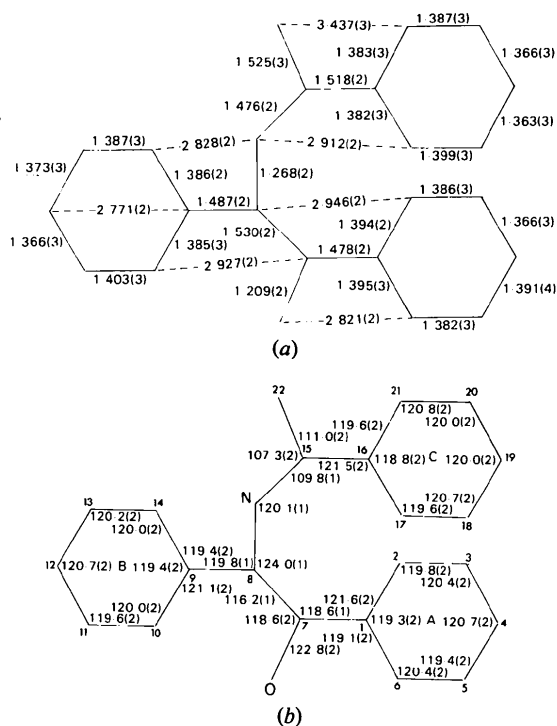|	x	y	z		x	y	z
C(1)	−3759 (1)	−5061 (2)	−3837 (2)	C(13)	−4353 (1)	−7628 (2)	−9468 (2)
C(2)	−3039 (1)	−5065 (2)	−4210 (2)	C(14)	−4174 (1)	−7841 (2)	−8022 (2)
C(3)	−2586 (1)	−4131 (2)	−3633 (3)	C(15)	−3494 (1)	−8375 (2)	−3611 (2)
C(4)	−2842 (1)	−3205 (2)	−2701 (3)	C(16)	−2696 (1)	−8340 (2)	−3333 (2)
C(5)	−3561 (1)	−3168 (2)	−2336 (2)	C(17)	−2219 (1)	−8917 (1)	−4282 (2)
C(6)	−4017 (1)	−4096 (2)	−2904 (2)	C(18)	−1488 (1)	−8871 (3)	−3978 (3)
C(7)	−4257 (1)	−6061 (2)	−4394 (2)	C(19)	−1244 (1)	−8293 (3)	−2738 (3)
C(8)	−3979 (1)	−7056 (2)	−5498 (2)	C(20)	−1714 (1)	−7751 (3)	−1777 (3)
C(9)	−4166 (1)	−6810 (2)	−7047 (2)	C(21)	−2439 (1)	−7762 (2)	−2078 (2)
C(10)	−4342 (1)	−5571 (2)	−7529 (2)	C(22)	−3799 (1)	−9725 (3)	−3299 (3)
C(11)	−4515 (1)	−5365 (2)	−8997 (2)	O	−4873 (1)	−6125 (2)	−4017 (2)
C(12)	−4525 (1)	−6397 (2)	−9938 (2)	N	−3639 (1)	−8079 (2)	−5155 (1)

Fig. 2. (a) Bond lengths (Å) and intramolecular distances (Å). (b) Atomic numbering and angles (°).

Table 4. Torsion angles (°) with their e.s.d.'s

C(2)–C(1)–C(7)–C(8)	−4·8 (2)
C(6)–C(1)–C(7)–C(8)	175·8 (1)
C(2)–C(1)–C(7)–O	175·4 (2)
C(6)–C(1)–C(7)–O	−4·0 (2)
C(1)–C(7)–C(8)–N	82·5 (2)
C(1)–C(7)–C(8)–C(9)	−101·0 (2)
O–C(7)–C(8)–N	−97·7 (2)
O–C(7)–C(8)–C(9)	78·8 (2)
C(7)–C(8)–C(9)–C(10)	22·5 (2)
C(7)–C(8)–C(9)–C(14)	−156·5 (2)
N–C(8)–C(9)–C(14)	20·1 (2)
N–C(8)–C(9)–C(10)	−160·9 (2)
C(7)–C(8)–N–C(15)	0·4 (2)
C(9)–C(8)–N–C(15)	−176·0 (1)
C(16)–C(15)–N–C(8)	−115·3 (1)
C(22)–C(15)–N–C(8)	123·9 (2)
C(17)–C(16)–C(15)–C(22)	74·3 (2)
C(21)–C(16)–C(15)–C(22)	−103·2 (2)
N–C(15)–C(16)–C(17)	−44·2 (2)
N–C(15)–C(16)–C(21)	138·2 (2)

The orientation of rings *A*, *B* and *C* is governed largely by the C···C distances (Fig. 2*a*), which are shorter than the sum of the van der Waals radii (3·4 Å for C···C; Pauling, 1960). The angles between the mean planes through each phenyl ring and the mean plane of the central skeleton are 21·9, 79·3 and 57·5° respectively.

Table 5. Least-squares planes with displacements of atoms (Å) from the planes and their e.s.d.'s

The equations of the best planes are expressed in orthogonal space as $PI + QJ + RK = S$.

Plane *A*: $-0·1876I + 0·5959J - 0·7809K = 0·9877$
Plane *B*: $0·9618I + 0·1695J - 0·2148K = -7·3099$
Plane *C*: $0·0826I + 0·8698J - 0·4865K = -6·3766$
Plane *D*: $0·8625I + 0·5024J - 0·0604K = -9·7664$

Plane A		Plane B	
C(1)	−0·0066 (17)	C(9)	0·0021 (16)
C(2)	0·0051 (18)	C(10)	−0·0062 (19)
C(3)	0·0023 (22)	C(11)	0·0073 (21)
C(4)	−0·0093 (24)	C(12)	−0·0038 (23)
C(5)	0·0037 (23)	C(13)	−0·0006 (23)
C(6)	0·0048 (19)	C(14)	0·0003 (21)
C(7)*	−0·0438 (16)	C(8)*	−0·0102 (15)

Plane C		Plane D	
C(16)	0·0058 (17)	C(7)	0·0008 (16)
C(17)	−0·0113 (20)	C(8)	−0·0017 (16)
C(18)	0·0079 (26)	N	0·0012 (14)
C(19)	0·0074 (26)	C(15)	−0·0009 (18)
C(20)	−0·0116 (26)	C(1)*	1·2900 (16)
C(21)	0·0007 (21)	C(9)*	−0·0904 (16)
C(15)*	−0·0243 (18)	C(16)*	1·2914 (17)
		C(22)*	−1·2068 (27)
		O*	−1·0506 (13)

Dihedral angles (°)

A ∧ B	84·9	A ∧ C	28·0	B ∧ C	70·7
A ∧ D	79·3	B ∧ D	21·9	C ∧ D	57·5

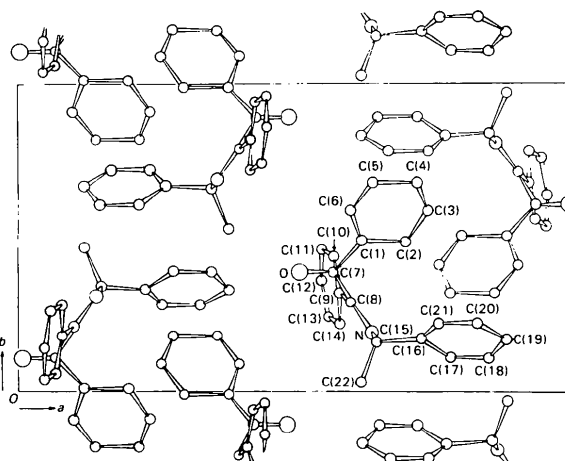* Not included in the calculation of the plane.

Fig. 3. Molecular packing viewed down *c*.

The phenyl rings are essentially planar, Table 5. The central skeleton C(7)–C(8)=N–C(15) is nearly flat, Table 4; coplanarity of the central skeleton and phenyl rings is precluded in part by the intramolecular repulsions (Tucker, Hoekstra, Ten Cate & Vos, 1975).

The average C—C distances in the phenyl rings *A*, *B*, *C* are 1·383 (3), 1·380 (3) and 1·386 (3) Å respectively. The length N=C(8) = 1·268 Å is in good agreement with that in *N*,*N*′-dibenzylidene-1,2-diphenylethylenediamine (Prelesnik & Nowacki, 1975).

Bond lengths involving H atoms are given in Table 3. The C—H lengths range from 0·88 to 1·12, mean 1·01 (3) Å.

As is shown in Table 2 the positional parameters correspond to the enantiomer of the molecule used to solve the structure. The asymmetric C(15) has an *S* configuration.

Fig. 3 shows the contents of the unit cell projected down *c*. There are no H atom intermolecular contacts <3·5 Å.

References

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature (London)*, 168, 271–272.
GARCÍA-RUANO, J. L. & PÉREZ-OSSORIO, R. (1975). *An. Quím.* 71, 93–97.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., 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.
MARTÍNEZ-RIPOLL, M. & FAYOS, J. (1977). *CONFAB*. Instituto Rocasolano, Serrano 119, Madrid-6, Spain.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
PRELESNIK, B. & NOWACKI, W. (1975). *Z. Kristallogr.* 142, 239–251.
TUCKER, P. A., HOEKSTRA, A., TEN CATE, J. M. & VOS, A. (1975). *Acta Cryst.* B31, 733–737.

Molecular and Crystal Structure of *meso*-(*RS*)-1,1,1,3,6,8,8,8-Octachlorooctane

BY J. C. J. BART*

Montedison Research Laboratories, Via S. Pietro 50, 20021 Bollate (Milano), Italy

AND I. W. BASSI AND M. CALCATERRA

Montedison 'G. Donegani' Research Laboratories, Via G. Fauser 4, Novara, Italy

Abstract

1,1,1,3,6,8,8,8-Octachlorooctane, $C_8H_{10}Cl_8$, crystallizes in space group $P2_1/n$ with $Z = 2$ and cell parameters $a = 6·269$ (5), $b = 15·546$ (16), $c = 7·947$ (6) Å, $\beta = 93·60$ (7)°. The crystal structure has been determined by X-ray diffraction techniques (857 observed reflections collected by an automatic diffractometer; final R value 0·049). The conformation of the molecule is governed by the steric and electrostatic interactions of the Cl atoms. Steric hindrance is minimized by the adoption of a nearly eclipsed conformation around the C_β–C_γ bonds (20° twist) and staggered conformations in other parts of the molecule. Strain is further relieved by slight angular deformations. C—Cl bond distances at tri- and monosubstituted C atoms differ significantly: 1·768 (average) and 1·800 (6) Å, respectively. Similarly, C_α–C_β is shorter [1·499 (7) Å] than other C—C bonds [average 1·528 (5) Å].

Introduction

Recently the addition reaction of carbon tetrachloride to 1,5-hexadiene using a redox-transfer initiating system has led to a highly chlorinated linear biadduct together with a cyclic monoadduct in low yield (Piccardi, Modena & Massardo, 1973). The main reaction product, 1,1,1,3,6,8,8,8-octachlorooctane, (I) has now been subjected to an X-ray crystal structure determination to establish the molecular conformation and to collect evidence for the bond-shortening effects of the electronegative substituents.

Experimental

The space group and preliminary cell parameters of (I) were obtained from Weissenberg photographs. Accurate cell dimensions and the orientation matrix were obtained from a least-squares fit of χ, φ, ω and 2θ values from 12 independent reflections measured on a four-circle diffractometer.

* Present address: Montedison 'G. Donegani' Research Laboratories, Via G. Fauser 4, Novara, Italy.