

C5—C6	1.520 (4)	C15—N16	1.459 (3)
C6—C7	1.542 (4)	N16—C17	1.455 (3)
C7—C8	1.528 (4)	C18—N19	1.136 (4)
C7—C17	1.530 (4)		
C2—N1—C6	113.5 (2)	C9—C8—C7	105.6 (2)
C2—N1—C10	112.2 (2)	C8—C9—C10	109.3 (2)
C6—N1—C10	110.8 (2)	C8—C9—C11	110.8 (2)
N1—C2—C18	110.4 (2)	C10—C9—C11	112.8 (2)
N1—C2—C20	111.6 (2)	N1—C10—C9	112.2 (2)
C18—C2—C20	108.1 (2)	N16—C11—C12	108.8 (2)
N1—C2—C3	110.2 (2)	N16—C11—C9	110.6 (2)
C18—C2—C3	107.7 (2)	C12—C11—C9	111.9 (2)
C20—C2—C3	108.8 (2)	C13—C12—C11	112.6 (3)
C4—C3—C2	112.3 (2)	C14—C13—C12	111.1 (3)
C5—C4—C3	108.8 (2)	C15—C14—C13	110.5 (3)
C4—C5—C6	112.9 (2)	N16—C15—C14	111.0 (3)
N1—C6—C5	112.3 (2)	C17—N16—C15	110.8 (2)
N1—C6—C7	109.5 (2)	C17—N16—C11	110.4 (2)
C5—C6—C7	110.9 (2)	C15—N16—C11	111.7 (2)
C8—C7—C17	109.0 (2)	N16—C17—C7	112.7 (2)
C8—C7—C6	109.0 (2)	N19—C18—C2	178.9 (3)
C17—C7—C6	113.0 (2)		

Acta Cryst. (1995). **C51**, 1160–1164

Conformationally Defined Cyclohexyl Carnitine Analogs

WAYNE J. BROUILLETTE, GARY M. GRAY* AND ASHRAF SAEED

Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294-1240, USA

(Received 24 January 1994; accepted 9 September 1994)

Abstract

Three diastereoisomers of racemic (3-carboxy-2-hydroxy-1-cyclohexyl)trimethylammonium chloride [C₁₀H₂₀NO₃⁺.Cl⁻; (1*S*,2*S*,3*S*) (2), (1*R*,2*S*,3*S*) (3) and (1*S*,2*R*,3*S*) (4)] were designed as rigid analogs for different low-energy conformational states of carnitine [(1), (3-carboxy-2-hydroxy-1-propyl)trimethylammonium chloride]. Structures (2)–(4) all assume a chair conformation in the solid state, in which the bulky trimethylammonio group occupies the equatorial position. As such, the orientations about C2—C3 in (2), (3) and (4) are all essentially the same as that found for (1) in the solid state (torsion angles for C1—C2—C3—N1 near 180°), while the orientations about C1—C2 in (2)–(4) are such that each diastereoisomer contains a different one of the three possible low-energy staggered conformations predicted for (1) in solution. Comparisons between (1) and (2)–(4) in the solid state revealed that diastereoisomers (2), (3) and (4) provide rigid models for the major low-energy conformations of carnitine.

Comment

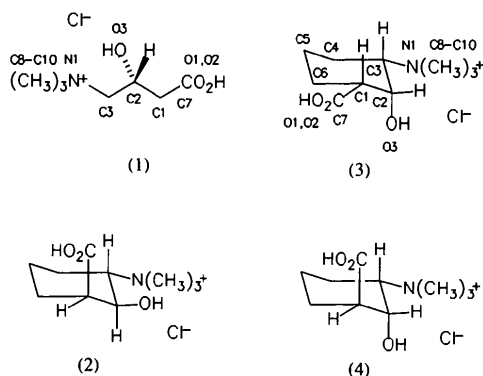
(*R*)-Carnitine (1) is important in cellular metabolism as a substrate for several different carnitine acyltransferases. Structure (1) is conformationally flexible and determining the protein-bound conformation for (1) with each of the acyltransferases is of considerable pharmacological interest. Studies by others (Colucci & Gandour, 1988) have suggested that protein-bound (1) contains a *gauche* relationship between N1 and O3 [atoms were numbered as in (2)–(4) for easy comparison]. This conformation about C2—C3 also exists in the crystal structure of (1) (Tomita, Urabe, Kim & Fujiwara, 1974) and is favored in solution (Colucci, Gandour & Mooberry, 1986). However, the protein-bound conformation for (1) about C1—C2 has not been determined and two of the three possible low-energy staggered conformations are nearly equally favored in solution (Colucci, Gandour & Mooberry, 1986). As part of a study to address this question, we synthesized racemic cyclohexyl carnitine analogs (2), (3) and (4) (Brouillette, Saeed, Abuelyaman, Hutchison, Wolkowicz & McMillin, 1994).

Data collection: *Kuma KM-4 User's Guide* (Kuma, 1992). Cell refinement: *Kuma KM-4 User's Guide*. Data reduction: *Kuma KM-4 User's Guide*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989). Software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances and angles involving H atoms, and torsion angles have been deposited with the IUCr (Reference: BK1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Borowiak, T., Bokii, N. G. & Struchkov, Yu. T. (1973). *Zh. Strukt. Khim.* **14**, 387–388.
- Katrusiak, A., Figas, E., Kałuski, Z. & Lesiewicz, D. (1989). *Acta Cryst.* **C45**, 1758–1760.
- Klyne, S., Scopes, P. N., Thomas, R. N., Skolik, J., Gawroński, J. & Wiewiórowski, M. (1974). *J. Chem Soc. Perkin Trans.* **1**, pp. 2565–2570.
- Kubicki, M., Borowiak, T. & Boczoń, W. (1991). *J. Crystallogr. Spectrosc. Res.* **21**, 575–579.
- Kuma (1992). *Kuma KM-4 User's Guide*. Version 6.0. Kuma Diffraction, Wrocław, Poland.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.
- Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Skolik, J., Krueger, P. J. & Wiewiórowski, M. (1970). *J. Mol. Struct.* **5**, 461–475.



It was anticipated that structures (2)–(4) would each exist in a ‘locked’ chair form, with the bulky trimethylammonio group occupying the equatorial position, thus providing conformationally rigid analogs of (1). Consequently, (2)–(4) each contain the desired *gauche* relationship between N1 and O3 but different low-energy staggered conformations about C1–C2. In order to confirm the relative stereochemical assignments and to assure that diastereoisomer (4), which contains two substituents in the axial position, does not favor a twisted-boat conformation in the solid state, the crystal structures for the hydrochloride salts of (2), (3) and (4) were solved.

Observed bond angles and distances in racemic (2), (3) and (4) are in relatively good agreement with those for (*R*)-carnitine (1). The exceptions are that the N1–C3 bond distance is longer and the N1–C3–C2 bond angle is narrower for racemates (2)–(4), presumably due to extra steric crowding from C4.

Among the selected torsion angles in Table 2, those given for (1) (except C2–C1–C7–O2) are of greatest interest since they define the spatial relationship between the carboxyl, hydroxyl and ammonio groups, which for (1) are involved in enzyme binding or enzymatic reaction. Comparison of these torsion angles indicates that the conformation of (3) most closely resembles that of (1) in the solid state, except that in (3) C7–C1–C2–O3 is about 23° smaller than in (1). The large deviation between (1) and (3) for C2–C1–C7–O2 (the carboxyl group orientation) likely results from differences in crystal packing forces. Racemic (2) and (4), like (3), also maintain the desired *gauche* relationship between N1 and O3. The deviation of the O3–C2–C3–N1 torsion angle from the ideal angle of 60° is largest in (4), which has two axial groups. Structures (2)–(4) each exhibit different low-energy staggered conformations about C1–C2 that were earlier predicted to predominate for (1) in solution (Colucci, Gandour & Mooberry, 1986), and the C7–C1–C2–O3 torsion angles are, in all cases, relatively close to the desired torsion angles of 60 or 180°. Structures (2)–(4) thus provide rigid structural models for the major low-

energy conformations of carnitine that are observed in the solid state and in solution.

For structures (2) and (3), intermolecular hydrogen bonding is similar to that observed for carnitine hydrochloride (1) (Tomita, Urabe, Kim & Fujiwara, 1974). In (1)–(3) the chloride ion mediates interactions between molecules by accepting a hydrogen bond from O1 of one molecule and O3 of the adjacent molecule. In structure (4) only the former hydrogen bond is observed.

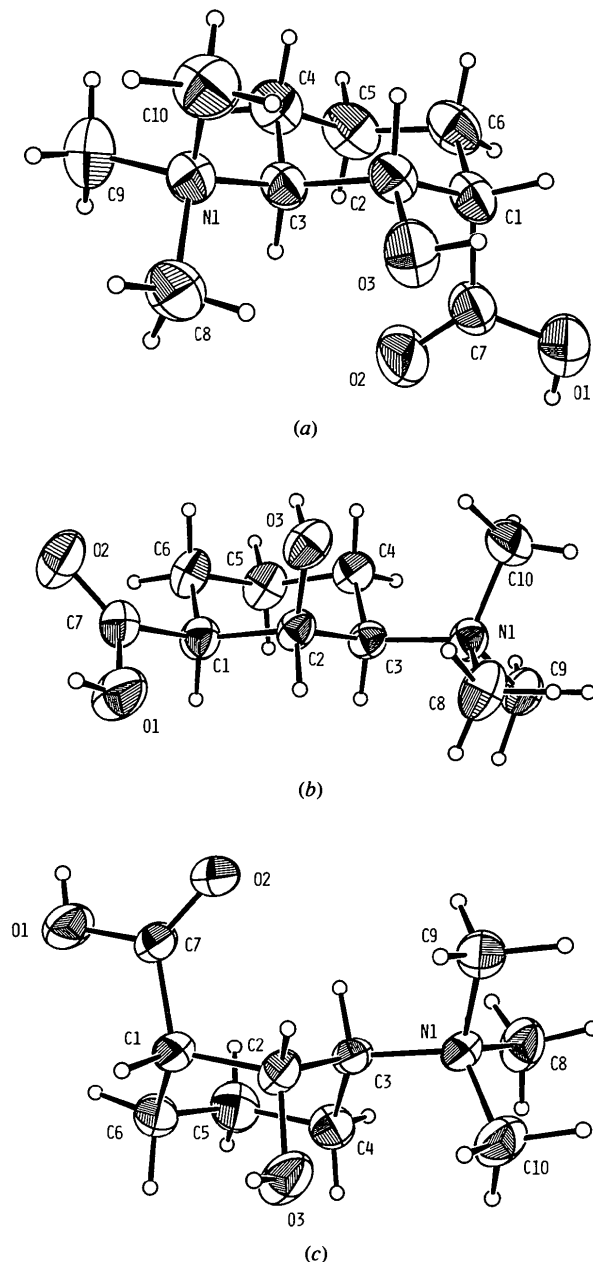


Fig. 1. Atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level for (a) (2), (b) (3) and (c) (4). H atoms are drawn with arbitrary radii.

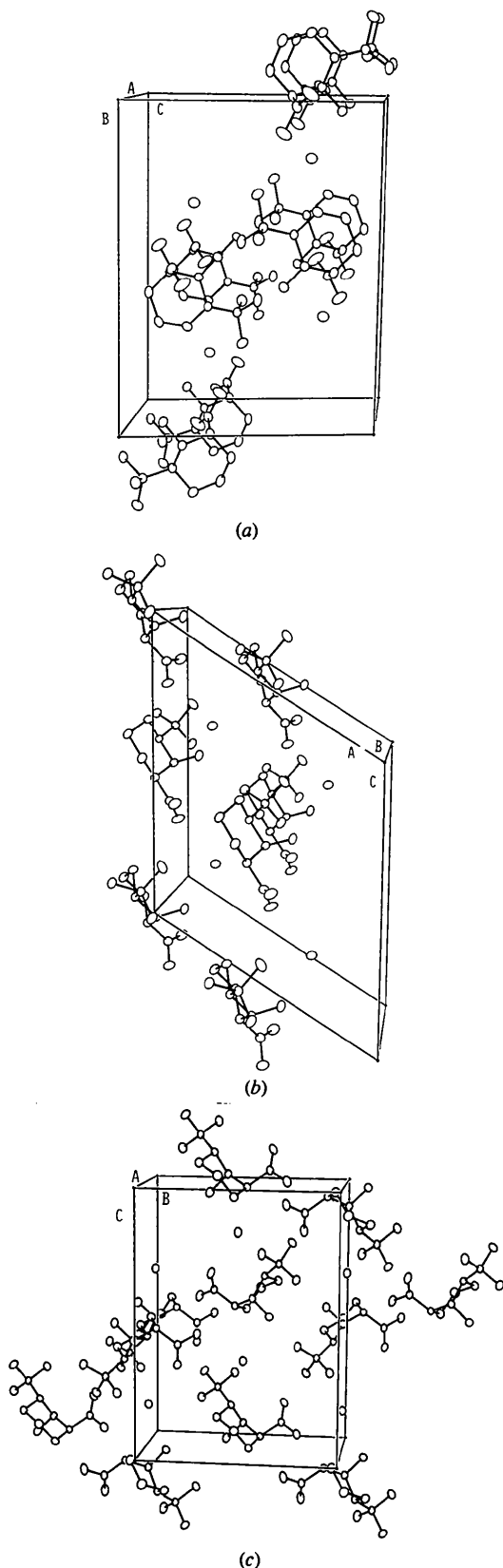


Fig. 2. The unit cell for (a) (2), (b) (3) and (c) (4).

Experimental

Crystals of racemic (2)–(4), which were synthesized by methods developed in our laboratory, were prepared by the slow vapor diffusion of diethyl ether into a saturated solution in ethanol. Melting points were (2) 522–522.5, (3) 479.5–481 and (4) 510–511 K. Crystals were cut to the appropriate sizes and then mounted on glass fibers with Super Glue gel.

Structure (2)

Crystal data

$C_{10}H_{20}NO_3^+.Cl^-$

$M_r = 237.73$

Monoclinic

$P2_1/n$

$a = 6.418 (1) \text{ \AA}$

$b = 15.864 (3) \text{ \AA}$

$c = 12.269 (2) \text{ \AA}$

$\beta = 102.38 (1)^\circ$

$V = 1220.2 (6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.293 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 25\text{--}35^\circ$

$\mu = 2.73 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Needle cut into block

$0.55 \times 0.49 \times 0.32 \text{ mm}$

Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω - 2θ scans

Absorption correction: empirical

$T_{\min} = 0.872$, $T_{\max} = 0.999$

2735 measured reflections

2665 independent reflections

1981 observed reflections

$[I \geq 3\sigma(I)]$

$\theta_{\max} = 74^\circ$

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 19$

$l = 0 \rightarrow 15$

3 standard reflections

frequency: 60 min

intensity decay: -4.0%

Refinement

Refinement on F

$R = 0.0507$

$wR = 0.0712$

$S = 2.172$

1981 reflections

195 parameters

Only coordinates of H atoms

refined (O–H 0.81–0.87,

C–H 0.85–1.05 \AA)

$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} = 0.02$

$\Delta\rho_{\max} = 0.251 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.301 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1963)

Extinction coefficient:

$1.5 (3) \times 10^{-6}$

Atomic scattering factors

from Cromer & Waber

(1974)

Structure (3)

Crystal data

$C_{10}H_{20}NO_3^+.Cl^-$

$M_r = 237.73$

Monoclinic

Cc

$a = 12.390 (1) \text{ \AA}$

$b = 8.245 (2) \text{ \AA}$

$c = 13.732 (1) \text{ \AA}$

$\beta = 121.543 (9)^\circ$

$V = 1195.6 (3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.321 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 25\text{--}35^\circ$

$\mu = 2.79 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Needle cut into block

$0.65 \times 0.62 \times 0.46 \text{ mm}$

Colorless

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω - 2θ scans
Absorption correction:
empirical
 $T_{\min} = 0.899$, $T_{\max} = 0.998$
1301 measured reflections
1272 independent reflections

Refinement

Refinement on F
 $R = 0.025$ (or 0.034)
 $wR = 0.0332$ (or 0.054)
 $S = 1.415$ (or 1.21)
1242 reflections
197 parameters
Only coordinates of H atoms
refined (O—H 0.76–0.79,
C—H 0.89–1.14 Å)
 $w = 1/\sigma^2(F_o)$

Structure (4)**Crystal data**

$C_{10}H_{20}NO_3^+ \cdot Cl^-$
 $M_r = 237.73$
Orthorhombic
 $P2_12_12_1$
 $a = 7.123$ (2) Å
 $b = 11.237$ (2) Å
 $c = 14.989$ (1) Å
 $V = 1199.7$ (4) Å³
 $Z = 4$
 $D_x = 1.316$ Mg m⁻³

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω - 2θ scans
Absorption correction:
empirical
 $T_{\min} = 0.940$, $T_{\max} = 1.00$
1468 measured reflections
1441 independent reflections

Refinement

Refinement on F
 $R = 0.030$ (or 0.045)
 $wR = 0.041$ (or 0.063)
 $S = 1.92$ (or 2.97)
1394 reflections
197 parameters
Only coordinates of H atoms
refined (O—H 0.74–0.80,
C—H 0.82–1.09 Å)
 $w = 1/\sigma^2(F_o)$

1242 observed reflections
 $[I \geq 3\sigma(I)]$
 $\theta_{\max} = 74^\circ$
 $h = -15 \rightarrow 0$
 $k = 0 \rightarrow 10$
 $l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: -0.1%

$(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 0.111$ e Å⁻³
 $\Delta\rho_{\min} = -0.043$ e Å⁻³
Extinction correction:
Zachariasen (1963)
Extinction coefficient:
 9.1 (7) $\times 10^{-6}$
Atomic scattering factors
from Cromer & Waber
(1974)

Cu $K\alpha$ radiation
 $\lambda = 1.5418$ Å
Cell parameters from 25
reflections
 $\theta = 25$ – 35°
 $\mu = 2.78$ mm⁻¹
 $T = 296$ K
Needle cut into block
 $0.73 \times 0.67 \times 0.60$ mm
Colorless

1394 observed reflections
 $[I \geq 3\sigma(I)]$
 $\theta_{\max} = 74^\circ$
 $h = -8 \rightarrow 0$
 $k = -14 \rightarrow 0$
 $l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: none

$(\Delta/\sigma)_{\max} = 0.02$
 $\Delta\rho_{\max} = 0.180$ e Å⁻³
 $\Delta\rho_{\min} = -0.239$ e Å⁻³
Extinction correction:
Zachariasen (1963)
Extinction coefficient:
 1.36 (3) $\times 10^{-5}$
Atomic scattering factors
from Cromer & Waber
(1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

Structure (2)	$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			B_{eq}
	x	y	z	
C1	0.1149 (1)	0.17031 (5)	0.27404 (7)	4.45 (2)
O1	-0.4738 (4)	0.0785 (2)	0.3517 (3)	6.41 (7)
O2	-0.5833 (4)	-0.0332 (2)	0.2520 (3)	6.85 (7)
O3	-0.1754 (4)	0.0226 (1)	0.1510 (2)	4.35 (5)
N1	-0.1685 (4)	-0.1512 (2)	0.0711 (2)	3.28 (5)
C1	-0.2087 (4)	-0.0190 (2)	0.3360 (2)	3.48 (5)
C2	-0.1299 (4)	-0.0438 (2)	0.2307 (2)	3.13 (5)
C3	-0.2248 (4)	-0.1281 (2)	0.1836 (2)	2.98 (5)
C4	-0.1569 (5)	-0.1958 (2)	0.2726 (3)	3.96 (6)
C5	-0.2450 (6)	-0.1735 (2)	0.3756 (3)	4.60 (7)
C6	-0.1636 (5)	-0.0888 (2)	0.4237 (2)	4.28 (7)
C7	-0.4432 (5)	0.0061 (2)	0.3069 (3)	3.83 (6)
C8	-0.3112 (6)	-0.1023 (2)	-0.0210 (3)	4.93 (8)
C9	-0.2070 (6)	-0.2431 (2)	0.0458 (3)	5.12 (8)
C10	0.0591 (5)	-0.1335 (2)	0.0693 (3)	4.65 (7)
HO1	-0.602 (7)	0.080 (3)	0.338 (4)	10†
HO3	-0.107 (5)	0.068 (2)	0.177 (3)	5.8†
Structure (3)				
C1	0.800	0.55262 (7)	0.800	3.93 (1)
O1	0.4919 (2)	1.1395 (2)	0.7411 (1)	4.55 (3)
O2	0.4699 (2)	0.9042 (2)	0.6537 (1)	4.54 (4)
O3	0.4059 (1)	1.2318 (2)	0.4771 (1)	3.36 (3)
N1	0.5599 (1)	1.4934 (2)	0.4574 (1)	2.72 (3)
C1	0.5988 (2)	1.1143 (3)	0.6419 (2)	2.89 (4)
C2	0.5312 (2)	1.2633 (2)	0.5667 (1)	2.54 (4)
C3	0.6153 (2)	1.3355 (2)	0.5259 (1)	2.44 (4)
C4	0.6464 (2)	1.2127 (3)	0.4617 (2)	3.08 (4)
C5	0.7172 (2)	1.0703 (3)	0.5410 (2)	3.46 (4)
C6	0.6372 (2)	0.9907 (3)	0.5826 (2)	3.32 (4)
C7	0.5141 (2)	1.0381 (3)	0.6784 (2)	3.11 (4)
C8	0.4944 (2)	1.5919 (3)	0.5029 (2)	3.83 (5)
C9	0.6686 (2)	1.5922 (3)	0.4698 (2)	3.38 (4)
C10	0.4696 (3)	1.4628 (3)	0.3326 (2)	4.49 (6)
HO1	0.444 (2)	1.096 (3)	0.751 (2)	4.4†
HO3	0.404 (3)	1.159 (4)	0.439 (2)	5.9†
Structure (4)				
C1	0.58061 (7)	1.00084 (4)	0.84718 (3)	3.532 (9)
O1	0.5995 (2)	0.7673 (1)	0.9472 (1)	4.18 (3)
O2	0.7885 (3)	0.6891 (1)	0.8454 (1)	5.13 (4)
O3	0.8533 (3)	0.3827 (1)	1.0015 (1)	4.55 (3)
N1	0.8584 (2)	0.3359 (1)	0.7992 (1)	2.61 (3)
C1	0.7066 (3)	0.5722 (2)	0.9737 (1)	2.72 (3)
C2	0.8288 (3)	0.4718 (2)	0.9352 (1)	2.74 (3)
C3	0.7285 (2)	0.4162 (2)	0.8553 (1)	2.39 (3)
C4	0.5453 (3)	0.3585 (2)	0.8852 (1)	3.28 (4)
C5	0.4209 (3)	0.4573 (2)	0.9230 (2)	3.87 (4)
C6	0.5120 (3)	0.5255 (2)	0.9991 (1)	3.57 (4)
C7	0.7022 (3)	0.6808 (2)	0.9142 (1)	2.75 (3)
C8	0.7489 (3)	0.2753 (2)	0.7267 (1)	3.97 (4)
C9	1.0040 (4)	0.4123 (2)	0.7548 (2)	4.38 (4)
C10	0.9558 (3)	0.2406 (2)	0.8516 (2)	3.90 (4)
HO1	0.603 (3)	0.819 (2)	0.916 (2)	5.4†
HO3	0.928 (3)	0.413 (2)	1.035 (2)	5.9†

† Fixed at 1.3 times the value of heavy atom to which it is bonded.

Table 2. Selected geometric parameters (Å, °)

Structure	(1) ^a	(2)	(3)	(4)
O1—C7	1.324 (10)	1.306 (4)	1.328 (3)	1.313 (2)
O2—C7	1.203 (10)	1.180 (4)	1.199 (3)	1.204 (3)
O3—C2	1.419 (10)	1.426 (3)	1.412 (2)	1.421 (2)
N1—C3	1.518 (10)	1.545 (4)	1.541 (2)	1.542 (2)
N1—C8		1.508 (4)	1.497 (4)	1.500 (3)
N1—C9		1.499 (4)	1.506 (3)	1.502 (3)
N1—C10		1.493 (4)	1.498 (3)	1.498 (3)
C1—C2	1.529 (11)	1.537 (4)	1.540 (3)	1.537 (3)

C1—C6		1.527 (4)	1.528 (4)	1.530 (3)
C1—C7	1.507 (11)	1.523 (4)	1.516 (4)	1.513 (3)
C2—C3	1.519 (11)	1.530 (4)	1.537 (3)	1.529 (2)
C3—C4		1.528 (4)	1.519 (3)	1.524 (3)
C4—C5		1.532 (6)	1.528 (3)	1.529 (3)
C5—C6		1.515 (4)	1.527 (4)	1.520 (3)
C3—N1—C8		109.0 (2)	111.6 (2)	110.4 (1)
C3—N1—C9		110.9 (2)	107.6 (1)	108.8 (1)
C3—N1—C10		112.7 (2)	112.6 (2)	114.2 (1)
C2—C1—C6		111.0 (2)	112.7 (2)	110.8 (1)
C2—C1—C7	111.5 (6)	110.9 (2)	109.0 (2)	112.5 (2)
C6—C1—C7		112.5 (3)	111.2 (2)	113.9 (2)
O3—C2—C1	108.7 (7)	109.3 (2)	113.7 (2)	108.9 (1)
O3—C2—C3	111.3 (7)	112.4 (2)	113.6 (2)	108.4 (1)
C1—C2—C3	107.2 (6)	111.4 (2)	108.6 (2)	109.3 (1)
N1—C3—C2	116.8 (7)	113.2 (2)	112.3 (2)	112.7 (1)
N1—C3—C4		112.7 (2)	112.1 (2)	115.2 (1)
O1—C7—O2	123.3 (8)	122.7 (3)	123.0 (3)	123.4 (2)
O1—C7—C1	111.8 (7)	111.2 (2)	111.5 (2)	112.7 (2)
O2—C7—C1	124.9 (7)	126.2 (3)	125.5 (3)	123.8 (2)
C2—C3—C4		108.4 (2)	112.3 (2)	110.1 (1)
C3—C4—C5		109.1 (3)	108.9 (2)	107.2 (2)
C4—C5—C6		111.6 (3)	110.7 (2)	113.4 (2)
C1—C6—C5		111.8 (2)	110.9 (2)	111.9 (2)
C6—C1—C2—C3		55.0 (3)	-53.6 (2)	56.6 (2)
C7—C1—C2—O3	73.4	53.9 (3)	-50.2 (2)	169.6 (2)
C7—C1—C2—C3	-166.2	-70.9 (3)	-177.6 (2)	-72.1 (2)
C2—C1—C6—C5		-51.4 (3)	54.5 (3)	-51.3 (2)
C2—C1—C7—O2	22.7	50.7 (4)	116.9 (2)	-1.83 (3)
O3—C2—C3—N1	-66.4	51.0 (3)	56.8 (2)	-74.9 (2)
C1—C2—C3—N1	174.8	174.1 (2)	-175.6 (1)	166.4 (1)
C1—C2—C3—C4		-60.1 (3)	57.0 (2)	-63.4 (2)
C2—C3—C4—C5		61.4 (3)	-60.2 (2)	62.2 (2)
C3—C4—C5—C6		-59.5 (3)	58.9 (2)	-57.0 (2)
C4—C5—C6—C1		54.4 (4)	-56.5 (2)	52.7 (2)
Cl···HO1	1.83	2.31 (4)	2.24 (4)	2.30 (3)
Cl···O1	3.00	2.988 (3)	2.973 (2)	3.025 (2)
Cl···HO3	2.23	2.31 (3)	2.40 (3)	5.96 (3) ^b
Cl···O3	3.06	3.168 (2)	3.130 (3)	5.246 (2) ^b
HO1···Cl···HO3	84	95 (1)	100 (1)	
O1···HO1···Cl	169	141 (4)	161 (3)	167 (3)
O3···HO3···Cl	138	168 (3)	153 (3)	

(a) Data from Tomita, Urabe, Kim & Fujiwara (1974). (b) Distances are much too long for hydrogen bonding.

The space groups for structures (2) ($P2_1/n$) and (4) ($P2_12_12_1$) were uniquely defined by their systematic absences. The space group for structure (3) (Cc) was not uniquely defined by the systematic absences but was proven to be correct by the successful structure refinement. The structure solutions and refinements were carried out using *MolEN* (Fair, 1990). Both linear decay corrections and empirical absorption corrections were applied to the data. The chloride ions were located in the Patterson maps and the remainder of the atoms were located by difference Fourier syntheses. All non-H atoms were refined anisotropically. The H atoms were also refined with fixed isotropic thermal parameters. Data were weighted using a non-Poisson scheme with an experimental uncertainty factor of 0.03 for all three structures. A secondary-extinction correction was applied and the extinction coefficient was refined. In the last stage of the refinements, no parameter varied by more than 0.02 of its standard deviation. The final difference Fourier maps had no interpretable peaks. For the noncentrosymmetric space groups of (3) and (4), both enantiomers were refined, and *R*, *wR* and *S* are reported for both refinements. Data and figures are for the enantiomers with the lower values. Corrections for anomalous dispersion were taken from Cromer (1974) and applied to the chloride ions.

ORTEP (Johnson, 1976) plots of (2), (3) and (4) are given in Figs. 1(a), 1(b) and 1(c), respectively. Unit-cell diagrams for (2), (3) and (4) are given in Figs. 2(a), 2(b) and 2(c). Note that, while (1) contains the (2*R*) configuration [numbered as in (2)–(4)], the configurations illustrated in Figs. 1(a–c) for (2)–(4) are (1*S*,2*S*,3*S*), (1*R*,2*S*,3*S*), and (1*S*,2*R*,3*S*), respectively.

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Program used to solve structure: *MolEN* (Fair, 1990). Program used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

This work was supported by a grant (HL44668) to WJB from the National Institutes of Health.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Brouillette, W. J., Saeed, A., Abuelyaman, A., Hutchison, T. L., Wolkowicz, P. E. & McMillin, J. B. (1994). *J. Org. Chem.* **59**, 4297–4303.
- Colucci, W. J. & Gandour, R. D. (1988). *Bioorg. Chem.* **16**, 307–334.
- Colucci, W. J., Gandour, R. D. & Mooberry, E. A. (1986). *J. Am. Chem. Soc.* **108**, 7141–7147.
- Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor: Kluwer Academic Publishers, Dordrecht.)
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Tomita, K., Urabe, K., Kim, Y. B. & Fujiwara, T. (1974). *Bull. Chem. Soc. Jpn.* **47**, 1988–1993.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1995). **C51**, 1164–1167

4,4'-Azoxydianisole at 203 K

CHAFIC CHEBLI AND FRANÇOIS BRISSE

Département de Chimie, Université de Montréal,
CP 6128, Succursale Centre-ville, Montréal, Québec,
Canada H3C 3J7

(Received 29 August 1994; accepted 25 October 1994)

Abstract

The crystal structure determination of the title compound, $C_{14}H_{14}N_2O_3$, reinvestigated using low-