C14*A*—H14*B*···Br1^{i}	2.60	3.692 (6)	178
C62*A*—H62*A*···Br2^{ii}	2.76	3.788 (7)	157
C14*A*—H14*A*···Br2^{ii}	2.71	3.782 (6)	169
C14*B*—H14C···Br1^{iii}	2.63	3.716 (6)	175
C62*B*—H62*B*···Br1^{iii}	3.13	4.009 (7)	138
C42*A*—H42*A*···Br1^{iv}	2.95	3.804 (8)	136
C33*B*—H33*B*···Br1^{v}	3.12	4.161 (8)	159
C53*B*—H53*B*···Br1^{vi}	3.16	4.089 (6)	143
C14*B*—H14D···Br2^{vii}	2.63	3.707 (6)	171
C61*B*—H61*B*···Br2^{vii}	2.99	3.948 (9)	147
C42*B*—H42*B*···Br2^{ii}	2.90	3.947 (8)	161
C53*A*—H53*A*···Br2^{viii}	3.04	3.976 (6)	144

Symmetry codes: (i) $x-\frac{1}{2},1-y,z$; (ii) $1-x,2-y,\frac{1}{2}+z$; (iii) $1-x,1-y,z-\frac{1}{2}$; (iv) $\frac{3}{2}-x,y,z-\frac{1}{2}$; (v) $\frac{1}{2}-x,1+y,z-\frac{1}{2}$; (vi) $1-x,2-y,z-\frac{1}{2}$; (vii) $x-\frac{1}{2},2-y,z$; (viii) $1-x,1-y,\frac{1}{2}+z$.

H-atom positions were refined in a riding model (*SHELXL*93; Sheldrick, 1993) with a C—H bond length of 1.09 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

The author is on leave from the Max-Delbrück-Centrum für Molekulare Medizin, Forschungsgruppe Kristallographie (Professor U. Heinemann), Berlin, Germany. He thanks Professor W. Saenger for giving him the opportunity to carry out this study in his laboratory and J. Jacob for measuring the IR data. The study was supported by the Deutsche Forschungsgemeinschaft (Sa 196/25–1).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lutz, B., van der Maas, J. & Kanters, J. A. (1994). *J. Mol. Struct.* **325**, 203–214.
North, A. C. T., Phillips, D. C. & Matthews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Steiner, Th. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2341–2342.
Steiner, Th. (1995). *Z. Kristallogr.* **210**, 459.

Acta Cryst. (1996). C**52**, 2266–2269

Glycyl-L-histidinium Chloride Dihydrate: an Unusual Histidine Conformation

THOMAS STEINER

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14159 Berlin, Germany. E-mail: steiner@chemie.fu-berlin.de

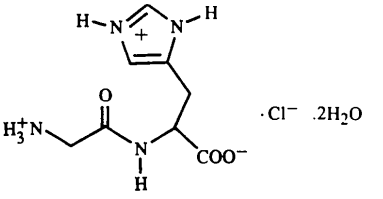
(*Received 23 February 1996; accepted 2 April 1996*)

Abstract

The histidine side chain of the title compound, $C_8H_{13}N_4O_3^+.Cl^-.2H_2O$, is protonated and is incorporated in a tight N—H···*X* and C—H···*X* hydrogen-bonding pattern. The orientation of the imidazole moiety is unusual and associated with a short intramolecular C—H···O=C hydrogen bond from HisCδ—H to the peptide C=O. This configuration has not been observed previously with peptides.

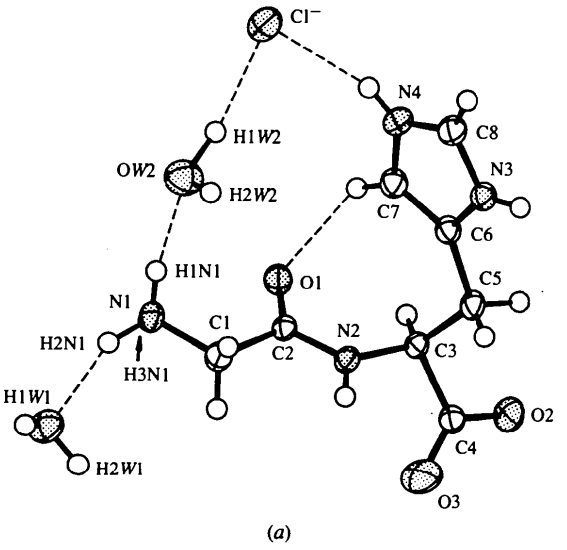
Comment

The crystal structure of the title compound, (1), was determined primarily to study the hydrogen-bonding interactions of the histidine residue. When carrying a positive charge, the imidazole moiety of histidine is often found tightly coordinated to hydrogen-bond acceptors. Not only both N—H but also both imidazole C—H groups then donate hydrogen bonds (see Steiner, 1995, 1996).

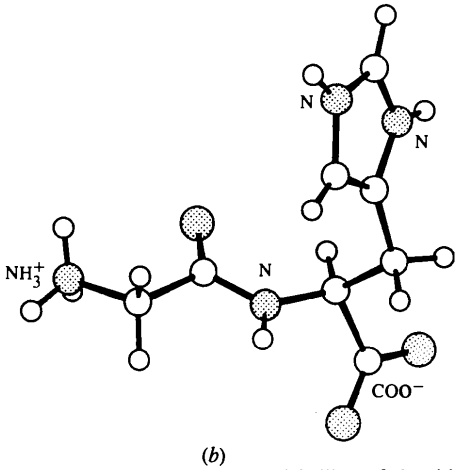


(1)

Compound (1) was crystallized as a mono hydrochloride so the dipeptide carries positive charges at the N terminus and at the histidine side chain, and a negative charge at the C terminus (Fig. 1*a*). There are two water molecules cocrystallized for every dipeptide. This leads to a complex system of O—H···*X*, N—H···*X* and C—H···*X* hydrogen bonds (*X* = O, Cl^-; Table 3) that need not be discussed here in detail. The hydrogen-bonding pattern formed by the imidazole moiety of (1) is shown in Fig. 2. As in previous studies, all N—H and C—H donors are engaged in hydrogen bonding, those donated by N3—H and C8—H even being three-centered. Most remarkable is a short intramolecular C—H···O hydrogen bond from C7—H (*i.e.* HisCδ—H) to the peptide C=O.



(*a*)



(*b*)

Fig. 1. (*a*) Molecular structure and atom labelling of the title compound. Displacement ellipsoids are drawn at the 50% probability level. (*b*) The Gly-His cation as observed in the crystal structure of Gly-L-His hemisuccinate monohydrate (Sridhar Prasad & Vijayan, 1993). The dipeptides are drawn in the same projection with respect to the peptide bonds. O and N atoms are shaded.

Recently, Sridhar Prasad & Vijayan (1993) reported the crystal structure of a different salt of the same peptide, glycyl-L-histidine hemisuccinate monohydrate (Fig. 1*b*). The conformation of the peptide backbone and the orientation of the bond C5—C6 (*i.e.* HisCβ—Cγ) is almost identical in both structures but the orientation of the histidine imidazole ring is very different. In (1), the torsion angle C3—C5—C6—C7 is $-15.1\,(4)°$, *i.e.* the imidazole ring is almost coplanar with C3—C5—C6 (Cα—Cβ—Cγ). This is associated with the short intramolecular C7—H···O=C hydrogen bond mentioned above (it is noted that such side-chain···main-chain C—H···O interactions may also occur in proteins). In the hemisuccinate salt, this torsion angle is 88.7°, *i.e.* the imidazole plane and Cα—Cβ—Cγ are perpendicular to each other, and all histidine

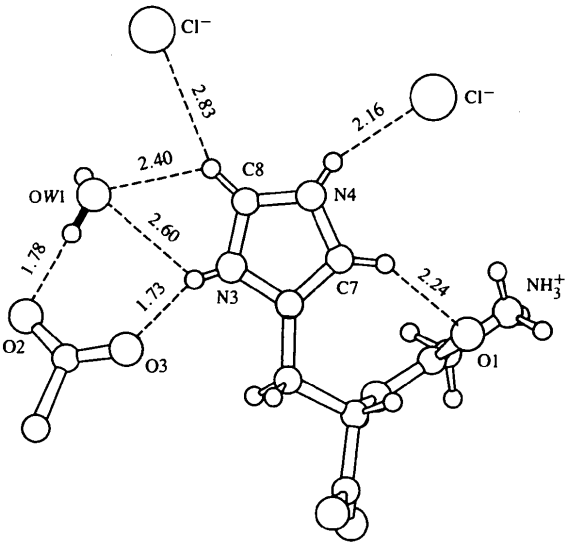


Fig. 2. The hydrogen-bonding pattern around the protonated histidine side chain, projection is on the imidazole plane. Numerical values of H···*X* distances are given for normalized H-atom positions.

N—H and C—H bonds point away from the backbone and are engaged in intermolecular hydrogen bonding.

To determine whether the histidine conformation of (1) is common or unusual, a comparative search of the Cambridge Structural Database (CSD) (Allen *et al.*, 1986) was performed (error-free crystal structures, $R < 0.08$, no disorder, no isomorphous structures). 30 histidine residues are found in 27 crystal structures. For all these residues, the imidazole ring is roughly perpendicular to Cα—Cβ—Cγ, as in Fig. 1(*b*). This is not affected by the rotation around the Cα—Cβ bond, which exhibits three principal types of orientation. Of the 30 histidine residues in the CSD, Cα—Cβ is oriented *trans* with respect to the Cα—CO bond in 14 cases, *trans* with respect to the Cα—H bond in a further 14 and *trans* with respect to the N—Cα bond in two cases. No previous example of an intramolecular HisCδ—H···O=C hydrogen bond like that in (1) is found in the small peptides archived in the CSD.

Experimental

The title compound (1) is commercially available (Sigma) and was recrystallized by vapour diffusion of EtOH into an aqueous solution of (1).

Crystal data

$C_8H_{13}N_4O_3^+.Cl^-.2H_2O$
$M_r = 284.71$
Orthorhombic
$P2_12_12_1$
$a = 4.8701\,(2)$ Å
$b = 11.0460\,(10)$ Å
$c = 23.877\,(4)$ Å
Cu $K\alpha$ radiation
$\lambda = 1.54176$ Å
Cell parameters from 25 reflections
$\theta = 8.2$–$39.2°$
$\mu = 2.860$ mm^{-1}
$T = 293\,(2)$ K

V = 1284.5 (3) Å^3
Z = 4
D_x = 1.472 Mg m^{-3}
D_m not measured

Rod
0.55 × 0.15 × 0.07 mm
Colourless

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Matthews, 1968)
T_{min} = 0.797, T_{max} = 0.999
2272 measured reflections
1912 independent reflections

1858 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0213
θ_{max} = 59.95°
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 12$
$l = -26 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 4.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0383
$wR(F^2)$ = 0.1357
S = 1.095
1898 reflections
231 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0777P)^2 + 0.1666P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002

$\Delta\rho_{max}$ = 0.231 e Å^{-3}
$\Delta\rho_{min}$ = −0.422 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.01 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cl	0.11377 (14)	0.98188 (6)	0.47838 (2)	0.0406 (2)
OW1	−0.9343 (4)	1.5549 (2)	0.42572 (9)	0.0381 (5)
OW2	−0.3876 (6)	1.1749 (2)	0.47778 (10)	0.0480 (6)
O1	−0.3634 (4)	1.19786 (15)	0.33331 (7)	0.0294 (4)
O2	−0.7339 (4)	1.0053 (2)	0.16492 (7)	0.0390 (5)
O3	−1.0116 (5)	1.1354 (2)	0.20597 (8)	0.0574 (7)
N1	−0.5772 (5)	1.3588 (2)	0.40452 (9)	0.0270 (5)
N2	−0.7760 (5)	1.1238 (2)	0.30465 (8)	0.0235 (4)
N3	−0.6462 (5)	0.7647 (2)	0.35879 (8)	0.0274 (5)
N4	−0.3234 (5)	0.8436 (2)	0.40701 (9)	0.0301 (5)
C1	−0.7711 (5)	1.2832 (2)	0.37260 (11)	0.0289 (6)
C2	−0.6148 (5)	1.1975 (2)	0.33472 (9)	0.0219 (5)
C3	−0.6716 (5)	1.0409 (2)	0.26237 (9)	0.0221 (5)
C4	−0.8189 (5)	1.0635 (2)	0.20612 (9)	0.0242 (5)
C5	−0.7169 (6)	0.9078 (2)	0.27915 (10)	0.0278 (6)
C6	−0.5747 (6)	0.8701 (2)	0.33191 (9)	0.0256 (6)
C7	−0.3725 (6)	0.9204 (2)	0.36263 (10)	0.0289 (6)
C8	−0.4911 (6)	0.7506 (2)	0.40396 (10)	0.0305 (6)

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.225 (3)	N4—C8	1.314 (4)
O2—C4	1.246 (3)	N4—C7	1.378 (3)
O3—C4	1.229 (3)	C1—C2	1.515 (3)
N1—C1	1.473 (3)	C3—C5	1.539 (3)
N2—C2	1.340 (3)	C3—C4	1.543 (3)
N2—C3	1.455 (3)	C5—C6	1.497 (4)
N3—C8	1.326 (3)	C6—C7	1.348 (4)
N3—C6	1.375 (3)		
C2—N2—C3	123.4 (2)	O3—C4—O2	125.8 (2)
C8—N3—C6	109.5 (2)	O3—C4—C3	117.5 (2)
C8—N4—C7	109.3 (2)	O2—C4—C3	116.7 (2)
N1—C1—C2	110.0 (2)	C6—C5—C3	114.7 (2)
O1—C2—N2	125.0 (2)	C7—C6—N3	106.3 (2)
O1—C2—C1	121.1 (2)	C7—C6—C5	133.0 (2)
N2—C2—C1	113.9 (2)	N3—C6—C5	120.8 (2)
N2—C3—C5	111.8 (2)	C6—C7—N4	107.0 (2)
N2—C3—C4	109.8 (2)	N4—C8—N3	107.9 (2)
C5—C3—C4	108.4 (2)		
N1—C1—C2—N2	179.1 (2)	N2—C3—C4—O2	174.4 (2)
N1—C1—C2—O1	−0.4 (3)	N2—C3—C5—C6	−61.5 (3)
C1—C2—N2—C3	175.0 (2)	C3—C5—C6—C7	−15.1 (4)
C2—N2—C3—C4	−125.3 (2)	C3—C5—C6—N3	164.7 (2)
C2—N2—C3—C5	114.4 (3)	C4—C3—C5—C6	177.4 (2)

Table 3. *Selected hydrogen-bond parameters (Å, °)*

Data for normalized H-atom positions are based on bond lengths of O—H = 0.98, N—H = 1.04 and C—H = 1.09 Å.

	D—H	H···A	D···A	D—H···A	H_{norm}···A
OW1—H1W1···Cl^i	0.77 (5)	2.48 (5)	3.202 (2)	157 (4)	2.29
OW1—H2W1···O2^{ii}	0.88 (5)	1.88 (5)	2.756 (3)	174 (4)	1.78
OW1—H2W1···O3^{ii}	0.88 (5)	2.71 (5)	3.278 (3)	123 (4)	2.66
OW2—H1W2···Cl	1.05 (6)	2.21 (6)	3.242 (3)	171 (4)	2.27
OW2—H2W2···Cl^{iii}	0.71 (4)	2.53 (4)	3.232 (3)	167 (4)	2.27
N1—H1N1···OW2	0.87 (3)	1.99 (4)	2.835 (3)	165 (3)	1.82
N1—H2N1···OW1	1.00 (4)	1.89 (4)	2.823 (3)	154 (3)	1.86
N1—H3N1···O2^{iv}	0.94 (4)	1.85 (4)	2.768 (3)	165 (3)	1.75
N2—HN2···O1^{iii}	0.82 (3)	2.27 (3)	3.053 (3)	160 (2)	2.06
N2—HN2···O3	0.82 (3)	2.37 (3)	2.624 (3)	99 (2)	2.34
N3—HN3···O3^v	0.78 (4)	1.96 (4)	2.684 (3)	154 (3)	1.73
N3—HN3···OW1^{vi}	0.78 (4)	2.71 (3)	3.145 (3)	117 (3)	2.60
N4—HN4···Cl	0.80 (3)	2.38 (3)	3.126 (2)	156 (2)	2.16
C1—H1C1···O2^{ii}	0.96 (3)	2.69 (3)	3.554 (3)	149 (2)	2.58
C3—HC3···O3^{vii}	1.04 (3)	2.63 (3)	3.638 (4)	162 (2)	2.59
C5—H2C5···O1^{viii}	0.96 (4)	2.63 (4)	3.570 (3)	167 (3)	2.50
C7—HC7···O1	0.92 (3)	2.38 (3)	3.144 (3)	141 (2)	2.24
C8—HC8···OW1^{vi}	0.96 (3)	2.47 (4)	3.099 (4)	123 (3)	2.40
C8—HC8···Cl^{ix}	0.96 (3)	2.95 (3)	3.840 (3)	156 (3)	2.83

Symmetry codes: (i) $x-\frac{3}{2}, \frac{5}{2}-y, 1-z$; (ii) $-2-x, y+\frac{1}{2}, \frac{1}{2}-z$; (iii) $x-1, y, z$; (iv) $-1-x, y+\frac{1}{2}, \frac{1}{2}-z$; (v) $-2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vi) $x, y-1, z$; (vii) $x+1, y, z$; (viii) $-1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ix) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

The author is on leave from the Max-Delbrück-Centrum für Molekulare Medizin, Forschungsgruppe Kristallographie (Professor U. Heinemann), Robert Rössle Strasse 10, D-13122, Berlin, Germany. He thanks Professor W. Saenger for the opportunity to carry out this study in his laboratory and the Deutsche Forschungsgemeinschaft for support (Sa 196/25–1).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Enraf–Nonius (1989). CAD-4 Software. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Matthews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sridhar Prasad, G. & Vijayan, M. (1993). *Acta Cryst.* B**49**, 348–356.
Steiner, Th. (1995). *Acta Cryst.* D**51**, 93–97.
Steiner, Th. (1996). *Acta Cryst.* C**52**, 1845–1847.

Acta Cryst. (1996). C**52**, 2269–2271

Half-Chair Conformation of *trans*-1,4-Dimethyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione

HIROSHI MORIWAKI,[a] TATSUYA KAWAMOTO[b] AND TAKUMI OSHIMA[a]*

[a]*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Toyonaka, Osaka 560, Japan, and* [b]*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. E-mail: oshima@ch.wani.osaka-u.ac.jp*

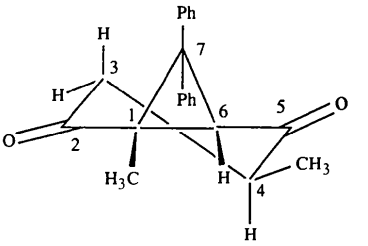
(*Received 8 November 1995; accepted 8 March 1996*)

Abstract

The structure of the title compound, $C_{21}H_{20}O_2$, was determined by X-ray analysis. The results revealed that the 2,5-dioxocyclohexane skeleton is in a half-chair conformation, with torsion angles C(2)—C(1)—C(6)—C(5) −1.5 (3) and C(2)—C(3)—C(4)—C(5) −36.5 (3)° on account of the fused cyclopropane ring which locates the 4-methyl group in an equatorial position. The plane of the *endo*-phenyl group was also found to be essentially parallel to the fused C(1)—C(6) bond.

Comment

The title compound, (1), was synthesized by the photo-induced hydrogenation of 2,5-dimethyl-1,1-diphenylhomobenzoquinone (Oshima, Tamada & Nagai, 1994). It underwent a fast H/D exchange at both the 3- and 4-positions when treated with methanol-[*d*]$_4$. This means that the compound obtained must necessarily attain the more stable configuration and conformation. An NMR study showed that the vicinal coupling constants of the 4-methine proton are J = 13.86 and 6.60 Hz with the adjacent methylene H atoms, suggesting a possible staggered conformation around the C(3)—C(4) bond (Hoch, Dobson & Karplus, 1985). However, the conjunction with the rigid cyclopropane ring seems to exert some steric effects on the conformation of the parent six-membered ring. Such effects would result in the deformation of the relevant ring system from the familiar chair form. Therefore, some ambiguity remains in the structure deduced from the NMR spectrum. In addition, compound (1) consists of a 2,5-dioxonorcarane framework with two trigonal carbonyl Csp^2 atoms for which the structural features are not well known. The X-ray structure analysis of (1) was thus carried out.



(1)

The X-ray crystal structure of (1) showed that the six-membered 2,5-dioxocyclohexane framework adopts a half-chair conformation, with torsion angles C(1)—C(2)—C(3)—C(4) 34.7 (3), C(2)—C(3)—C(4)—C(5) −36.5 (3), C(3)—C(4)—C(5)—C(6) 20.4 (3), C(4)—C(5)—C(6)—C(1) −1.7 (3), C(2)—C(1)—C(6)—C(5) −1.5 (3) and C(6)—C(1)—C(2)—C(3) −15.1 (3)°, owing to the fused cyclopropane ring. Therefore, the larger coupling constant (13.86 Hz) can be ascribed to the axial-H(3*A*)–axial-H(4) coupling and the smaller (6.60 Hz) to the equatorial-H(3*B*)–axial-H(4) coupling, as indicated by the torsion angles H(3*A*)—C(3)—C(4)—H(4) −154.4 (4) and H(3*B*)—C(3)—C(4)—H(4) −37.0 (3)°.

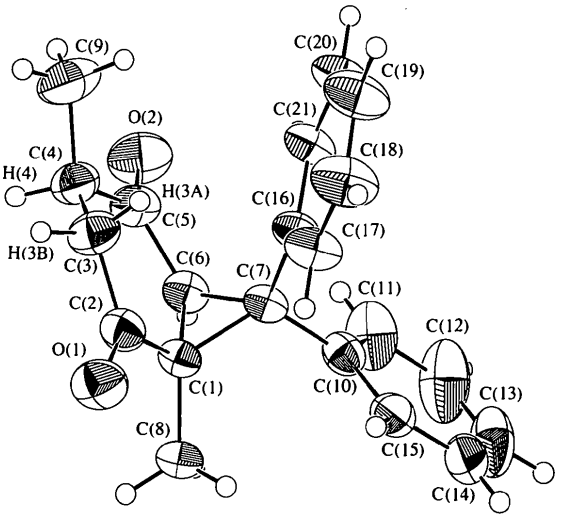


Fig. 1. A view of the title molecule with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.