Refinement

Refinement on F
$R = 0.0286$
$wR = 0.0345$
$S = 3.901$
1073 reflections
67 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$
$(\Delta/\sigma)_{\max} = <0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—S2	2.0398 (8)	S3—C3	1.731 (2)
S1—C1	1.818 (2)	C1—C1^{i}	1.521 (4)
S2—C2	1.741 (2)	C2—C3	1.316 (3)
S3—C1	1.817 (2)		
S2—S1—C1	99.18 (6)	S1—C1—C1^{i}	113.5 (2)
S1—S2—C2	100.48 (8)	S3—C1—C1^{i}	113.0 (2)
C1—S3—C3	106.75 (9)	S2—C2—C3	125.7 (2)
S1—C1—S3	111.13 (9)	S3—C3—C2	132.5 (2)

Symmetry code: (i) $-x, -y, 1 - z$.

The weak reflections [$I < 10\sigma(I)$] were rescanned (maximum five times) and the counts were accumulated to assure good counting statistics. The structure was solved by the direct methods *SHELXS*86 program (Sheldrick, 1985) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). The positions of all H atoms were determined from the difference Fourier synthesis map and refined isotropically. The non-H atoms were refined anisotropically. All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985, 1992) and *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement.

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas and General Scientific Research from the Ministry of Education, Science and Culture, Japan.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1429). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Block, R. & Jansen, L. (1985). *J. Chem. Phys.* **82**, 3322–3328.
Dixon, D. A., Zeroka, D., Wendoloski, J. J. & Wasserman, Z. R. (1985). *J. Phys. Chem.* **89**, 5334–5336.
Molecular Structure Corporation (1985, 1992). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rauk, A. (1984). *J. Am. Chem. Soc.* **106**, 6517–6524.
Sato, R. (1990). *Rev. Heteroatom Chem.* **3**, 193–210, and references therein.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Shimizu, T., Iwata, K. & Kamigata, N. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 2357–2359.
Shimizu, T., Iwata, K., Kamigata, N. & Ikuta, S. (1997). *J. Chem. Res.* (*S*), 38–39; *J. Chem. Res.* (*M*), 344–354.

Acta Cryst. (1997). C**53**, 749–751

2,5-Diaziridinyl-3-phenyl-*p*-benzoquinone

Rob H. J. Hargreaves,[a] Stephen P. Mayalarp,[a] John Butler,[a] Moses Lee[b] and William T. Pennington[c]

[a]*CRC Department of Biophysical Chemistry, Paterson Institute for Cancer Research, Christie Hospital NHS Trust, Wilmslow Road, Manchester M20 9BX, England,* [b]*Department of Chemistry, Furman University, Greenville, SC 29613, USA, and* [c]*Department of Chemistry, Clemson University, Clemson, SC 29634-1905, USA. E-mail: xraylab@clemson.edu*

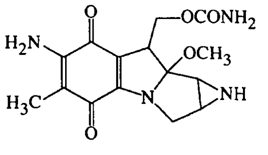
(*Received 11 November 1996; accepted 24 January 1997*)

Abstract

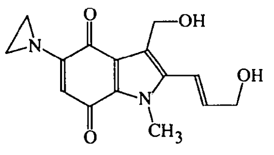
The crystal structure of the title compound, $C_{16}H_{14}N_2O_2$, a novel anticancer agent, has been determined at 295 (1) K. The aziridine rings form approximately regular triangles, with N—C distances of 1.442 (5)–1.456 (5) Å, C—C distances of 1.462 (6) and 1.467 (6) Å, C—N—C angles of 60.5 (3) and 60.7 (3)°, and C—C—N angles of 59.7 (3)–60.1 (3)°. The aziridine ring planes make dihedral angles of 48.1 (3) and 48.3 (3)° with the quinone ring. The dihedral angle between the quinone ring plane and the phenyl ring is 49.8 (2)°. The molecules are linked by C—H$\cdots X$ hydrogen bonding into bilayers which stack along the c axis; C$\cdots$O distances range from 3.355 (4) to 3.631 (5) Å and the unique C$\cdots$N distance is 3.427 (5) Å.

Comment

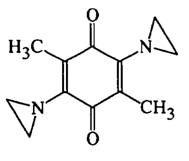
Mitomycin C (MC) is an important clinical anticancer agent which is effective for the treatment of a wide range of solid tumors (Crooke & Bradner, 1976; Powis, 1987; Verweij & Pinedo, 1990). Its significant biological activity has, in part, been attributed to its selective activation in cancerous tissues by reducing enzymes, such as DT-diaphorase (DTD) (Siegel, Gibson, Preusch & Ross, 1990). Marked elevation in DT-diaphorase activity and mRNA content have been documented in both preneoplastic and established cancers (Malkinson *et al.*, 1992). With these discoveries, there has been an intense effort to develop cytotoxic agents that are good substrates of DT-diaphorase. Among them, the antitumor quinones, streptonigrin, EO9, MeDZQ and the most recently synthesized analogue PDZQ (Beall *et al.*, 1992) have been shown to be excellent substrates for recombinant and rat DTD (Beall *et al.*, 1992). Although PDZQ is highly cytotoxic against H460 human non-small cell lung cancer cells which are rich in DTD activity, it is also quite cytotoxic against H596 cells which are devoid of DTD activity. The reasons for this apparent lack of biological selectivity of PDZQ are unclear, but may include alternative routes of bioactivation in H596 cells or chemical activation. There is presently a concerted effort to elucidate the biological mechanism of PDZQ and in this communication we report the unambiguous determination of its structure.



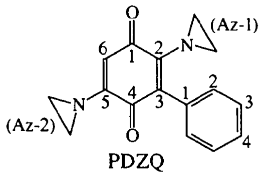
MC



EO9



MeDZQ



PDZQ

The molecular geometry in PDZQ compares well with that of related compounds such as 2,5-bis(ethyleneimino)-1,4-benzoquinone (Ito & Sakurai, 1973) and 2-(4-methoxyphenyl)-1,4-benzoquinone (Desiraju, Paul & Curtin, 1977). The packing of PDZQ molecules in the crystal (Fig. 2) is influenced by weak C—H···*X* hydrogen bonding. Contacts range from 3.355 (4) to 3.631 (5) Å for C···O interactions and there is a C···N interaction of 3.427 (5) Å. Although some of these contacts fall slightly outside the range reported for similar contacts (Taylor & Kennard, 1982), they possess reasonable geometry for this type of interaction.

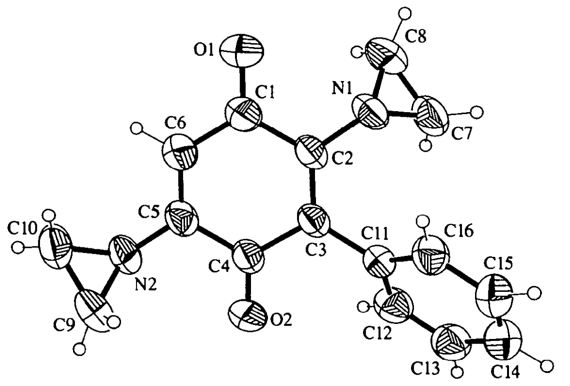


Fig. 1. The molecular structure of PDZQ showing 50% probability displacement ellipsoids.

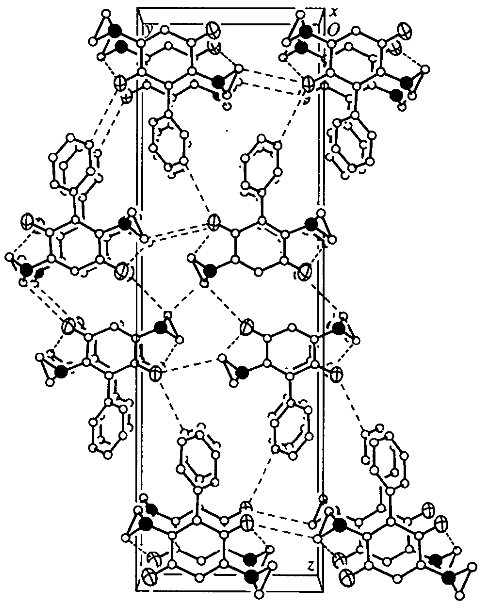


Fig. 2 Packing diagram viewed down the *a* axis.

Experimental

PDZQ was synthesized as a red solid in 26% yield by the reaction of aziridine with phenyl-1,4-quinone in dry ethanol. X-ray quality crystals were grown by slow evaporation of a solution of the compound in hexane–methylene chloride (10:1). The crystal used for analysis was mounted with epoxy onto the end of a glass fiber. The ^1H and ^{13}C NMR spectra of PDZQ were measured at room temperature on a Bruker AM-300 spectrometer in $CDCl_3$ with TMS as an internal standard (δ 0 p.p.m). The ^{13}C NMR [δ 114.9 (C6), 125.9 (Ph-1), 127.7 (Ph-3), 127.9 (Ph-4), 130.8 (Ph-2), 131.3 (C3), 151.3 and 156.4 (C2 and C5), 181.9 and 183.4 (C1 and C4)] and ^1H NMR signals [δ 2.02 (*s*, 4H, Az-1), 2.08 (*s*, 4H, Az-2), 6.05 (*s*, 1H, H6), 7.35–7.5 (*m*, 5H, Ph)] ruled out the possibility of 2,3-diaziridinylated PDZQ, but could not distinguish between the 2,5- and 2,6- isomers.

Crystal data

$C_{16}H_{14}N_2O_2$
$M_r = 266.29$
Orthorhombic
$P2_12_12_1$
$a = 5.0997\ (9)$ Å
$b = 9.1740\ (10)$ Å
$c = 28.375\ (5)$ Å
$V = 1327.5\ (4)$ Å^3
$Z = 4$
$D_x = 1.332$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 48 reflections
$\theta = 25.31–49.21°$
$\mu = 0.724$ mm^{-1}
$T = 295\ (1)$ K
Plate
0.28 × 0.11 × 0.10 mm
Red

Data collection

Siemens *R*3*m*/*V* diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1990)
$T_{\min} = 0.82$, $T_{\max} = 0.93$
1354 measured reflections
1354 independent reflections
831 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 65°$
$h = 0 \rightarrow 6$
$k = -10 \rightarrow 0$
$l = 0 \rightarrow 33$
3 standard reflections every 97 reflections intensity decay: 7.0%

Refinement

Refinement on F^2
$R(F) = 0.0451$
$wR(F^2) = 0.1094$
$S = 1.029$
1354 reflections
183 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.159$ e Å^{-3}
$\Delta\rho_{\min} = -0.158$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0023 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 1.5 (8)

Table 1. *Selected bond lengths (Å)*

O1—C1	1.228 (4)	C1—C2	1.492 (6)
O2—C4	1.223 (4)	C2—C3	1.358 (4)
N1—C2	1.387 (4)	C3—C4	1.479 (5)
N1—C7	1.455 (6)	C3—C11	1.490 (5)
N1—C8	1.456 (5)	C4—C5	1.495 (6)
N2—C5	1.394 (4)	C5—C6	1.332 (5)
N2—C9	1.442 (5)	C8—C7	1.467 (6)
N2—C10	1.454 (6)	C9—C10	1.462 (6)
C1—C6	1.443 (5)		

Table 2. *Contact distances (Å)*

C8···O2^{i}	3.570 (4)	C10···N2^{v}	3.427 (5)
C8···O1^{ii}	3.542 (4)	C10···O1^{vi}	3.376 (4)
C9···O2^{iii}	3.528 (4)	C15···O2^{vii}	3.355 (4)
C9···O1^{iv}	3.631 (5)		

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

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically and H atoms were generated with ideal geometries (C—H = 0.96 Å) and refined as riding groups with a single group displacement parameter [$U_H = 0.086(4)$ Å^2].

Data collection: *P*3 *Software* (Siemens, 1989). Cell refinement: *P*3 *Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

Financial support from the Cancer Research Campaign (to SPM) and the Medical Research Council of the United Kingdom (to RHJH) is gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1183). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beall, H. D., Murphy, A. M., Siegel, D., Hargreaves, R. H. J., Butler, J. & Ross, D. (1996). *Mol. Pharmacol.* **48**, 499–504.
Crooke, S. T. & Bradner, W. T. (1976). *Cancer Treat. Rev.* **3**, 121–139.
Desiraju, G. R., Paul, I. C. & Curtin, D. Y. (1977). *J. Am. Chem. Soc.* **99**, 1594–1601.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Ito, T. & Sakurai, T. (1973). *Acta Cryst.* **B29**, 1594–1603.
Malkinson, A. M., Siegel, D., Forest, G. L., Gadazar, A. F., Oie, H. K., Chan, D. C., Bunn, P. A., Mabry, M., Dykes, D. J., Harrison, S. D. Jr & Ross, D. (1992). *Cancer Res.* **52**, 4754–4757.
Powis, G. (1987). *Pharmacol. Ther.* **35**, 57–162.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.2. *Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siegel, D., Gibson, N. W., Preusch, C. & Ross, D. (1990). *Cancer Res.* **50**, 7483–7489.
Siemens (1989). *P3 Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Verweij, J. & Pinedo, H. B. (1990). *Anti-Cancer Drugs*, **1**, 5–13.

Acta Cryst. (1997). C**53**, 751-753

Benzyltrimethylammonium Tetramethoxoborate

WILLIAM CLEGG, R. JOHN ERRINGTON AND CLAIRE J. CARMALT

Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England. E-mail: w.clegg@ncl.ac.uk

(Received 16 January 1997; accepted 3 March 1997)

Abstract

In the title compound, $C_{10}H_{16}N^+.C_4H_{12}BO_4^-$ or $[PhCH_2NMe_3][B(OMe)_4]$, the anion has essentially $\bar{4}2m$ (D_{2d}) symmetry, with a tetragonal elongation to give two opposite O—B—O angles markedly smaller than the other four. Comparison with the structures of other salts indicates that this is an intrinsic property of the anion rather than the result of specific interionic or intermolecular interactions.

Comment

In the course of our investigations into non-aqueous polyborate chemistry, we have synthesized an organic salt of tetramethoxoborate, $[B(OMe)_4]^-$, as a soluble building block. The benzyltrimethylammonium salt, (I), is readily prepared from $B(OMe)_3$ and $[PhCH_2NMe_3]$-$[OMe]$ in methanol.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997