The cyclopentene ring is almost planar with the largest internal torsion angle being $1\cdot4$ (3)° and the maximum deviation from the least-squares plane being $0\cdot008$ (3) Å. The interplanar angle between the cyclopentene ring and C(6)C(7)C(11)C(12) is $120\cdot2$ (2)°. C(6)C(13)C(12) symmetrically bridges the six-membered ring forming interplanar angles of $124\cdot4$ (2) and $124\cdot0$ (2)° with C(6)C(7)C(11)C(12) and C(6)-C(5)C(1)C(12), respectively. This bridge is significantly asymmetric in 8,9,10-trinorbornene molecules exhibiting pyramidalization of the sp^2 C atoms. The $119\cdot9$ (2)° interplanar angle between the 8,9,10-trinorbornane unit C(6)C(5)C(1)C(12) and C(1)S(2)-S(4)C(5) is the same as that between the cyclopentene ring and the 8,9,10-trinorbornane moiety.

The intramolecular distances between *endo* H atoms, H(1)···H(11) and H(5)···H(7), are $2\cdot38$ (3) and $2\cdot37$ (3) Å respectively. H(132) lies $3\cdot00$ (3) and $2\cdot95$ (2) Å from S(2) and S(4) and $3\cdot95$ (2) Å from S(3). The only significant intermolecular contact is $2\cdot27$ (4) Å between H(1) atoms of adjacent molecules. The X-ray structural data are consistent with the addition of the S_3 unit to the *exo* face of the 8,9,10-trinorbornene molecule forming a nonplanar five-membered trithiolane ring with the central sulfur *anti* with respect to the methylene bridge. The *exo* addition is consistent with the pyramidalization of the sp^2 C atoms of 8,9,10-trinorbornene (Watson, 1983).

References

BARTLETT, P. D. & GHOSH, T. (1985). In preparation.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
DAVIES, D. I. (1970). *Essays on Free-Radical Chemistry*, Spec. Publ. No. 24, edited by W. A. WATERS & D. H. HEY, pp. 201–237. London: The Chemical Society.
EMSLEY, J., GRIFFITHS, D. W. & JAYNE, G. J. J. (1979). *J. Chem. Soc. Perkin Trans.* 1, pp. 228–232.
EMSLEY, J., GRIFFITHS, D. W. & OSBORN, R. (1979). *Acta Cryst.* B35, 2119–2121.
INOUE, S., TEZUKA, T. & OAE, S. (1978). *Phosphorus Sulfur*, 4, 219–221.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
KATO, A., HASHIMOTO, Y., OTSUKA, I. & NAKATSU, K. (1978). *Chem. Lett.* pp. 1219–1222.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
MOORE, C. G. & SEVILLE, R. W. (1954). *J. Chem. Soc.* pp. 2082–2089.
NAYLOR, R. F. (1947). *J. Chem. Soc.* pp. 1532–1539.
PRYOR, W. A. (1962). *Mechanisms of Sulfur Reaction*, pp. 97–116. New York: McGraw-Hill.
SHIELDS, T. C. & KURTZ, A. N. (1969). *J. Am. Chem. Soc.* 91, 5415–5416.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
WATSON, W. H. (1983). In *Stereochemistry and Reactivity of Systems Containing π Electrons*. Deerfield Beach, Florida: Verlag Chemie International.

Structure of 1,2'-Spirobiindan-1',3'-dione, a Key Intermediate in the Total Synthesis of Fredericamycin A*

BY K. R. ACHARYA, VEDAVATI G. PURANIK, S. S. TAVALE AND T. N. GURU ROW†

Physical Chemistry Division, National Chemical Laboratory, Pune – 411 008, India

Abstract. $C_{17}H_{12}O_2$, $M_r = 248\cdot3$, monoclinic, $P2_1/n$, $a = 12\cdot544$ (2), $b = 7\cdot507$ (1), $c = 13\cdot480$ (2) Å, $\beta = 97\cdot09$ (1)°, $V = 1259\cdot7$ Å³, $Z = 4$, D_m(flotation in aq. KI) $= 1\cdot312$, $D_x = 1\cdot309$ Mg m⁻³, λ(Mo $K\alpha$) $= 0\cdot7107$ Å, $\mu = 0\cdot94$ mm⁻¹, $F(000) = 520\cdot0$, $T =$ 293 K, $R = 0\cdot050$ for 651 observed reflections. The [4.4]nonane system is characteristic of fredericamycin A. The angle between the two aromatic portions at the spiro C [$89\cdot9$ (6)°] imposes the necessary spatial requirements and the C=O bond lengths [$1\cdot216$ (9) and $1\cdot202$ (9) Å] indicate that they are properly positioned for synthesis of fredericamycin A. The internal angles at the spiro C atom average $102\cdot4$ (6)°.

Introduction. Fredericamycin A (Fig. 1a, Misra, Pandey & Silverton, 1982) is an antitumour antibiotic which possesses a novel spiro[4.4]nonane system. This characteristic spatial imposition may have a role in determining its biological activity. The title compound (Fig. 1b) was prepared as a part of the total synthesis of fredericamycin A (Rama Rao, Reddy & Deshpande, 1984). It was imperative to establish the structure unequivocally by single-crystal studies.

Experimental. Crystal (colourless) of approximate dimensions 0·23 × 0·25 × 0·25 mm used for data collection, lattice parameters from 22 reflections (14 < 2θ < 28°), intensity data collected on an Enraf–Nonius CAD-4F-11M single-crystal X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation, three standard reflections ($70\bar{1}$, $61\bar{2}$, $41\bar{2}$), <4% intensity variation, $\omega/2\theta$ scan mode, scan speed 1° min⁻¹, θ < 24°, 2219 reflections collected, 651 judged significant ($|F_o| \geq 3\sigma|F_o|$), h 0–14, k 0–8, k 0–±15, no correction for absorption, structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix refinement of scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from difference map) converged to $R = 0·050$, $wR = 0·048$, $S = 1·24$, $\sum w(|F_o|-|F_c|)^2$ minimized, $w = (3·5 + 1·0|F_o| + 0·025|F_o|^2)^{-1}$, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), max. $\Delta/\sigma = 0·1$, final $\Delta\rho$ excursions <|0·2|e Å⁻³, *LALS* (Gantzel, Sparks & Trueblood, 1961) used for refinement.

Discussion. The atomic parameters with their standard deviations for non-H atoms are given in Table 1.* Bond lengths and angles are given in Table 2. Fig. 2 gives a perspective view of the molecule along with the numbering of atoms. The spiro system in the title

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42583 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters for non-H atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å²)
O(1)	3883 (4)	1809 (9)	4671 (4)	6·37
O(2)	363 (4)	1978 (8)	5495 (4)	5·71
C(1)	3028 (6)	1365 (12)	4933 (5)	4·84
C(2)	2855 (5)	−130 (10)	5600 (4)	4·46
C(3)	1811 (5)	−96 (12)	5846 (4)	3·97
C(4)	1235 (5)	1443 (12)	5354 (6)	4·58
C(5)	1933 (4)	2254 (10)	4632 (5)	4·31
C(6)	1521 (5)	1739 (11)	3566 (5)	3·63
C(7)	1151 (6)	3251 (12)	2975 (7)	5·60
C(8)	1295 (7)	4857 (11)	3535 (8)	7·40
C(9)	1916 (7)	4365 (13)	4570 (8)	7·68
C(10)	3571 (6)	−1420 (13)	6004 (6)	5·14
C(11)	3228 (7)	−2665 (9)	6665 (6)	6·00
C(12)	2173 (6)	−2626 (11)	6865 (5)	5·26
C(13)	1466 (5)	−1329 (11)	6490 (5)	4·84
C(14)	1443 (5)	69 (11)	3158 (5)	4·08
C(15)	1014 (6)	−195 (13)	2176 (6)	6·33
C(16)	677 (7)	1237 (17)	1632 (7)	6·83
C(17)	725 (5)	2917 (12)	1972 (7)	5·76

Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

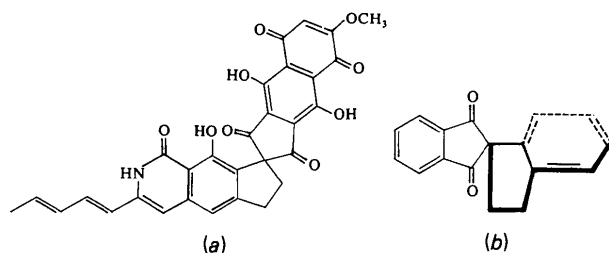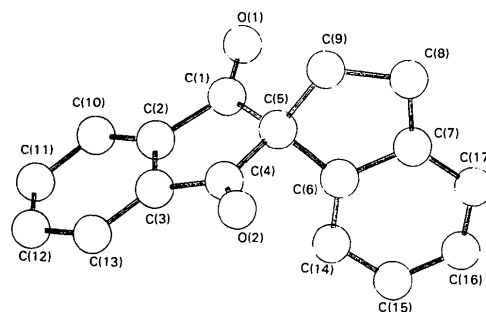|			
O(1)–C(1)	1·216 (9)	C(6)–C(7)	1·431 (12)
O(2)–C(4)	1·202 (9)	C(6)–C(14)	1·368 (11)
C(1)–C(2)	1·472 (11)	C(7)–C(8)	1·422 (13)
C(1)–C(5)	1·537 (10)	C(7)–C(17)	1·414 (13)
C(2)–C(3)	1·391 (9)	C(8)–C(9)	1·557 (15)
C(2)–C(10)	1·386 (11)	C(10)–C(11)	1·396 (12)
C(3)–C(4)	1·476 (11)	C(11)–C(12)	1·382 (12)
C(3)–C(13)	1·375 (10)	C(12)–C(13)	1·371 (11)
C(4)–C(5)	1·515 (10)	C(14)–C(15)	1·381 (10)
C(5)–C(6)	1·516 (10)	C(15)–C(16)	1·340 (15)
C(5)–C(9)	1·587 (12)	C(16)–C(17)	1·341 (15)
O(1)–C(1)–C(2)	126·0 (7)	C(6)–C(5)–C(9)	101·8 (6)
O(1)–C(1)–C(5)	126·6 (7)	C(5)–C(6)–C(7)	112·0 (6)
C(2)–C(1)–C(5)	107·3 (6)	C(5)–C(6)–C(14)	127·9 (6)
C(1)–C(2)–C(3)	110·2 (6)	C(7)–C(6)–C(14)	120·1 (7)
C(1)–C(2)–C(10)	129·5 (7)	C(6)–C(7)–C(8)	111·4 (7)
C(3)–C(2)–C(10)	120·3 (6)	C(6)–C(7)–C(17)	116·8 (7)
C(2)–C(3)–C(4)	109·4 (6)	C(8)–C(7)–C(17)	131·8 (8)
C(2)–C(3)–C(13)	121·1 (6)	C(7)–C(8)–C(9)	107·0 (8)
C(4)–C(3)–C(13)	129·5 (7)	C(5)–C(9)–C(8)	106·6 (7)
O(2)–C(4)–C(3)	126·5 (7)	C(2)–C(10)–C(11)	118·9 (7)
O(2)–C(4)–C(5)	125·2 (7)	C(10)–C(11)–C(12)	119·3 (7)
C(3)–C(4)–C(5)	108·3 (6)	C(11)–C(12)–C(13)	122·3 (7)
C(1)–C(5)–C(4)	103·0 (6)	C(3)–C(13)–C(12)	118·2 (7)
C(1)–C(5)–C(6)	109·2 (6)	C(6)–C(14)–C(15)	121·2 (7)
C(1)–C(5)–C(9)	116·9 (6)	C(14)–C(15)–C(16)	118·0 (8)
C(4)–C(5)–C(6)	110·5 (6)	C(15)–C(16)–C(17)	124·8 (9)
C(4)–C(5)–C(9)	115·5 (6)		

Fig. 1. (a) Fredericamycin A. (b) Title compound.

Fig. 2. A perspective view of the molecule.

compound is characteristic of that in fredericamycin A (Fig. 1a, Misra et al., 1982). The bond lengths C(1)–O(1) and C(4)–O(2) [1·216 (9) and 1·202 (9) Å respectively] indicate that the carbonyl groups are properly positioned for further synthesis. The distribution of bond lengths and angles around the 'spiro' atom C(5) shows some interesting features. The internal angle in both the five-membered rings at C(5) [average angle 102·4 (6)°] compares well with the theoretical value of 103·4° obtained in a VF calculation on (S)-(−)-spiro[4.4]nonane-1,6-dione (Altona, de Graaff, Leeuwestein & Romers, 1971). However, the bond lengths around the spiro C atom show larger variations [from 1·52 (1) to 1·59 (1) Å] than those predicted by the theoretical calculations [1·519 to 1·529 Å]. It is clear that the large variations in the title compound arise from steric interactions between the atoms in the neighbourhood of the spiro junction and also from the forced aromatic nature of the two parts of the molecule. The angle between these two planes is 89·9 (6)° which provides the necessary spatial requirements for further synthetic feasibility towards fredericamycin A.

References

ALTONA, C., DE GRAAFF, R. A. G., LEEUWESTEIN, C. H. & ROMERS, C. (1971). J. Chem. Soc. Chem. Commun. pp. 1305–1307.
GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). LALS. A program for the full-matrix least-squares refinement of positional, thermal and scale factors. Univ. of California, Los Angeles.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
MISRA, R., PANDEY, R. C. & SILVERTON, J. V. (1982). J. Am. Chem. Soc. 104, 4478–4479.
RAMA RAO, A. V., REDDY, D. R. & DESHPANDE, V. H. (1984). J. Chem. Soc. Chem. Commun. pp. 1119–1120.

Structures of a Series of Sulfonate Disubstituted Diacetylenes. III. 4,6-Decadiynylene Bis(pentamethylbenzenesulfonate)

BY RICHARD J. DAY, DAVID BLOOR, DAVID J. ANDO AND PHILIP A. NORMAN

Department of Physics, Queen Mary College, Mile End Road, London E1 4NS, England

MICHAEL B. HURSTHOUSE AND MAJID MOTEVALLI

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, England

AND HARRY W. MILBURN, ELIZABETH BLAIR AND ALAN R. WERNINCK

Department of Chemistry, Napier College of Commerce and Technology, Colinton Road, Edinburgh EH10 5DT, Scotland

Abstract. $C_{32}H_{42}O_6S_2$, $M_r = 586.80$, monoclinic, $C2/c$, $a = 21.632$ (3), $b = 18.669$ (2), $c = 15.063$ (2) Å, $\beta = 97.65$ (1)°, $U = 6029.0$ Å^3, $Z = 8$, $D_m(300\,\text{K}) = 1.29$ (1), $D_x = 1.29$ Mg m^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1.5418$ Å, $\mu = 1.836$ mm^{-1}, $F(000) = 2512$, $T = 300$ K, final $R = 0.0463$ for 2766 counter reflections. The molecule adopts a Z-shaped conformation with the aromatic rings on either side of the diacetylene group. The lack of solid-state polymerization for this compound is a consequence of this molecular conformation, which sterically inhibits any topochemical reaction of the diacetylene moieties in adjacent molecules.

Introduction. This paper forms part of a series in which we correlate crystal structure and solid-state reactivity of diacetylenes with substituent groups containing sulfonate groups. Details of the background to these studies are given in the first paper in the series (Werninck, Blair, Milburn, Ando, Bloor, Motevalli & Hursthouse, 1985).

Experimental. Title compound (PMDD) prepared by the general method reported previously (Ando, Bloor, Hubble & Williams, 1980). Recrystallization from methanol gave a white crystalline solid (C = 65·13,