Monensin benzyl ester (1c): IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.85–2.27 (identical with parent monensin, 45 H), 2.67 (br s, 1 H), 2.71 (m, 1 H), 3.25 (s, 3 H), 3.46 (m, 2 H), 3.59 (m, 2 H), 3.76 (m, 1 H), 3.80 (dd, 1 H, J = 3.1, 10.0 Hz), 3.86 (d, 1 H, J = 4.7 Hz), 3.88 (br s, 1 H), 4.05 (dd, 1 H, J = 2.3, 9.1 Hz), 4.28 (m, 1 H), 4.38 (d, 1 H, J = 9.3 Hz), 5.14 (d, 1 H, J = 12.4 Hz), 5.20 (d, 1 H, J = 12.3 Hz), 7.30–7.39 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{43}H_{68}O_{11} - 2H_2O + H$ 725.4629, found 725.4692.

Monensin *o*-fluorobenzyl ester (1d): IR ($CHCl_3$) 1710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.84–2.28 (identical with parent monensin, 45 H), 2.70 (m, 1 H), 2.79 (br s, 1 H), 3.25 (s, 3 H), 3.46 (br s, 2 H), 3.57 (m, 2 H), 3.74 (m, 1 H), 3.81 (dd, 1 H, J = 3.0, 10.0 Hz), 3.87 (d, 1 H, J = 4.7 Hz), 4.00 (br s, 1 H), 4.05 (dd, 1 H, J = 2.5, 8.9 Hz), 4.28 (m, 1 H), 4.43 (d, 1 H, J = 8.9 Hz), 5.20 (d, 1 H, J = 12.7 Hz), 5.26 (d, 1 H, J = 12.2 Hz), 7.06 (m, 1 H), 7.13 (m, 1 H), 7.28–7.32 (m, 1 H), 7.43 (m, 1 H); FAB-HRMS (m/e calcd for $C_{43}H_{67}O_{11}F + Na$ 801.4565, found 801.4445.

Monensin pentafluorobenzyl ester (1e): IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.84–2.28 (identical with parent monensin, 45 H), 2.69 (m, 1 H), 2.72 (br s, 1 H), 3.29 (s, 3 H), 3.46 (br s, 2 H), 3.56–3.60 (m, 2 H), 3.75 (m, 1 H), 3.82 (dd, 1 H, J = 3.2, 9.8 Hz), 3.88 (d, 1 H, J = 4.5 Hz), 4.03 (dd, 1 H, J = 2.3, 9.0 Hz), 4.04 (br s, 1 H), 4.29 (m, 1 H), 4.44 (br s, 1 H), 5.25 (s, 2 H); FAB-HRMS (m/e) calcd for $C_{43}H_{63}O_{11}F_5 + Na$ 873.4188, found 873.4233.

Lasalocid benzyl ester (2b): IR ($CHCl_3$) 1650, 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.76–2.25 (identical with parent lasalocid, 36 H), 2.20 (s, 3 H), 2.77–2.88 (m, 4 H), 3.19 (d, 1 H, J = 2.2 Hz), 3.42 (br s, 1 H), 3.44 (dd, 1 H, J = 2.2, 11.9 Hz), 3.74–3.84 (m, 3 H), 5.39 (d, 1 H, J = 12.1 Hz), 5.41 (d, 1 H, J = 11.9 Hz), 6.64 (d, 1 H, J = 7.5 Hz), 7.14 (d, 1 H, J = 7.9 Hz), 7.34–7.45 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{41}H_{60}O_8 + H$ 681.4366, found 681.4357.

Salinomycin benzyl ester (3b): IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.68–2.43 (identical with parent salinomycin, 50 H), 1.42 (s, 3 H), 2.20 (m, 1 H), 2.39 (m, 1 H), 2.44 (br s, 1 H), 2.74 (m, 1 H), 3.00 (d, 1 H, J = 5.6 Hz), 3.05 (m, 1 H), 3.18 (m, 1 H), 3.59 (dd, 1 H, J = 2.6, 10.4 Hz), 3.67 (br t, 1 H, J = 9.3 Hz), 3.82 (q, 1 H, J = 6.9 Hz), 3.90 (d, 1 H, J = 9.3 Hz), 4.00 (br d, 1 H, J = 8.9 Hz), 4.06 (dd, 1 H, J = 5.3, 5.9 Hz), 4.12 (m, 1 H), 5.34 (d, 1 H, J = 12.4 Hz), 5.39 (d, 1 H, J = 12.6 Hz), 5.98 (br d, 1 H, J = 10.7 Hz), 6.08 (dd, 1 H, J = 2.1, 10.7 Hz), 7.28–7.45 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{49}H_{76}O_{11} - H_2O + H$ 823.5360, found 823.5369.

Nigericin benzyl ester (4b): IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.86–2.55 (identical with parent nigericin, 53 H), 3.27 (m, 1 H), 3.33 (s, 3 H), 3.52–3.60 (m, 3 H), 3.79 (dd, 1 H, J = 2.1, 10.5 Hz), 3.84 (m, 1 H), 3.90 (d, 1 H, J = 4.2 Hz), 4.23 (m, 1 H), 4.31 (m, 1 H), 4.95 (br s, 1 H), 5.10 (d, 1 H, J = 12.5 Hz), 5.23 (d, 1 H, J = 12.5 Hz), 7.29–7.37 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{47}H_{74}O_{11} + K$ 853.4868, found 853.4847.

Ion-Selective Electrode Experiments. Electrode cells of the type Ag; AgCl, KCl(saturated)/0.3 M NH_4NO_3/sample solution/membrane/0.01 M NaCl, AgCl; Ag [membrane composition: 1 wt % potassium tetrakis(*p*-chlorophenyl)borate, 3 wt % ionophore, 30 wt % poly(vinyl chloride), 66 wt % dibenzyl ester] were used for electromotive force (emf) measurements. The membrane prepared was mounted on a DKK membrane electrode body to form an ion-selective electrode. Each emf was measured at pH = 3.0 ± 0.1 with an Orion Research EA 920 ion analyzer. The values obtained were set into the Nicolsky-Eisenman equation for calculation by the separate solution method.[14]

Method of Evaluation for Stability Constants. The stability constant (K) for 1:1 complexation is defined in eq 1, where

$$K = [C]/\{[I]_o - [C]\}\{[G]_o - [C]\} \tag{1}$$

[C], $[I]_o$, and $[G]_o$ represent the concentration of complex in the equilibrated state, initial concentration of ionophore, and initial concentration of guest, respectively. Supposing that guest-induced change in the chemical shift of proton signal ($\Delta\delta$) can be related to $\Delta\delta_\infty$ (saturated $\Delta\delta$) as in eq 2. Thus, one can derive eq 3.

$$\Delta\delta = [C]\Delta\delta_\infty/[I]_o \tag{2}$$

$$\Delta\delta = [[I]_o + [G]_o + 1/K - \{([I]_o + [G]_o + 1/K)^2 - 4[I]_o[G]_o\}^{1/2}]/(2[I]_o/\Delta\delta_\infty) \tag{3}$$

Substituting measured $\Delta\delta$, $[I]_o$, and $[G]_o$ values in eq 3, we determined the stability constant (K) by nonlinear least-squares treatment (Gauss–Newton method). Curves indicated in Figure 1 were computer-calculated titration curves according to eq 3.

Acknowledgment. We are grateful to Professor Kazuhiro Maruyama of Kyoto University and Professor Tatsuo Higashiyama of Okayama University for valuable discussions. We also express our gratitude to the SC-NMR Laboratory of Okayama University for 500-MHz ^1H NMR experiments. This research was supported in part by Grants-in-Aid for Scientific Research on Priority Areas ("Multiplex Organic System") and for Encouragement of Young Scientists from the Ministry of Education, Science, and Culture, Japan. Financial support from Shimadzu Science Foundation is also appreciated.

Supplementary Material Available: ^1H and/or ^{13}C NMR spectra for compounds **1c–e**, **2b**, **3b**, and **4b** (20 pages). Ordering information is given on any current masthead page.

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[14] Moody, G. J.; Thomas, J. D. R. In *Selective Ion-Sensitive Electrodes*; Merrow: Herts, 1971.

1,4-Dimethyl-9,10-anthraquinodimethane: Molecular and Crystal Structure of a Simple Quinodimethane

Stuart Rosenfeld*

Department of Chemistry, Smith College, Northampton, Massachusetts 01063

Jerry P. Jasinski

Department of Chemistry, Keene State College, Keene, New Hampshire 03431

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Quinodimethanes have proven to be extremely useful intermediates for the synthesis of cyclophanes[1] and other compounds. Their propensity toward cyclodimerization, polymerization, and Diels–Alder chemistry,[2] while an advantage in synthetic applications, creates challenges for those engaged in structural studies. Nonetheless, numerous reports of the spectroscopic characteristics of these compounds at low temperatures, including electronic,[3] vibrational,[3] nuclear magnetic resonance,[4] and photoelectron[5] spectroscopy, have appeared. Theoretical approaches, particularly molecular orbital calculations, have also amplified understanding of the chemistry and structure of these labile molecules.[6] A number of isolable 9,10-anthraquinodimethanes, e.g., **1**[7] and **2**,[8,9] have been

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[1] Keehn, P. M., Rosenfeld, S. M., Eds. *Cyclophanes*; Academic Press: New York, 1983.

[2] See, for example: Miller, I. T.; Richards, K. E. *J. Chem. Soc. C* **1967**, 855.

[3] (a) Pearson, J. M.; Six, H. A.; Williams, D. J.; Levy, M. *J. Am. Chem. Soc.* 1971, *93*, 5034. (b) Pebalk, A. V.; Barashkov, N. N.; Kozlov, Yu. A.; Kardash, I. Ye; Provednikov, A. N. *Polymer Sci. USSR* **1981**, *23*, 2933.

[4] Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436.

[5] Allan, M.; Heilbronner, E.; Kaupp, G. *Helv. Chim. Acta* **1976**, *59*, 1949.

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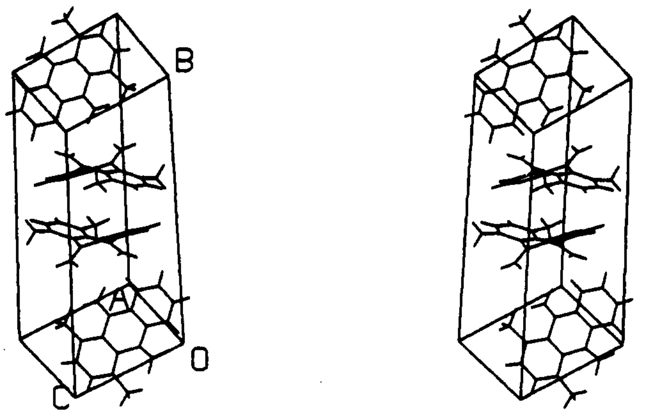
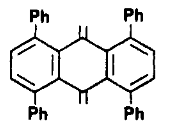
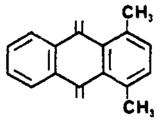


Figure 1. Stereo packing diagram for 1,4-dimethyl-9,10-anthraquinodimethane (**2**).

described briefly in the literature and a dipole moment measurement for **1** has provided convincing evidence that **1** has a nonplanar geometry. Surprisingly, there are apparently no reports to date of X-ray crystal structures of any of these isolable quinodimethanes.[10] We now report the first such structure determination, namely, that of **2**.



1



2

The structure of quinodimethane **2**[11] was determined by X-ray structure analysis on a clear prism[12] isolated by crystallization from wet acetone. There are four molecules in the unit cell (Figure 1), and the molecular geometry and numbering scheme appear in Figure 2. The four molecules are identical, all being the same one of two possible conformational enantiomers. Positional and isotropic thermal parameters are given in Table I. The central ring of **2** has a boat geometry, and the angle between the least-squares planes of the aromatic rings is 37.39°.[12] The expected bond length alternation is present (Table II) and bond lengths are in good agreement with previously calculated (SCF MO) values for 9,10-anthraquinodimethane.[6a] The exocyclic double bonds are 1.34-Å long, reflecting the lack of significant delocalization. Bond angles are given in Figure 3, from which it is apparent that even in this highly bent geometry there is appreciable steric interaction between the vinyl and peri methyl groups as evidenced by expansion of the C15–C1–C13 and C13–C9–C17 angles and their symmetry related partners.

Table I. Positional Parameters and Isotropic Thermal Parameters (B, Å^2)[19] for 2

atom	x	y	z	B (eq)
C(1)	0.2790 (8)	0.1034 (2)	0.7881 (6)	4.8 (3)
C(2)	0.237 (1)	0.0519 (3)	0.8593 (7)	5.8 (3)
C(3)	0.069 (1)	0.0197 (3)	0.8089 (7)	6.5 (3)
C(4)	−0.0714 (8)	0.0383 (2)	0.6855 (6)	4.6 (3)
C(5)	−0.1201 (8)	0.1399 (2)	0.1864 (7)	4.9 (3)
C(6)	−0.022 (1)	0.1695 (3)	0.0799 (7)	5.9 (3)
C(7)	0.140 (1)	0.2041 (3)	0.1332 (7)	6.0 (3)
C(8)	0.2069 (8)	0.2075 (2)	0.2944 (7)	5.1 (3)
C(9)	0.1683 (7)	0.1783 (2)	0.5770 (6)	4.1 (2)
C(10)	−0.1622 (7)	0.1134 (2)	0.4686 (6)	3.9 (2)
C(11)	−0.0568 (7)	0.1423 (2)	0.3487 (6)	3.9 (2)
C(12)	0.1096 (7)	0.1763 (2)	0.4030 (6)	3.8 (2)
C(13)	0.1373 (7)	0.1236 (2)	0.6627 (6)	3.9 (2)
C(14)	−0.0342 (7)	0.0903 (2)	0.6102 (6)	4.1 (2)
C(15)	0.475 (1)	0.1343 (3)	0.8425 (8)	7.0 (4)
C(16)	−0.244 (1)	−0.0023 (3)	0.6330 (8)	6.4 (3)
C(17)	0.2335 (8)	0.2282 (3)	0.6482 (8)	5.4 (3)
C(18)	−0.3612 (8)	0.1101 (1)	0.4475 (8)	5.5 (3)
H(2)	0.341 (7)	0.042 (2)	0.950 (6)	7 (1)
H(3)	0.042 (6)	−0.011 (2)	0.864 (5)	5 (1)
H(5)	−0.236 (7)	0.116 (2)	0.148 (6)	7 (1)
H(6)	−0.066 (8)	0.170 (3)	−0.046 (7)	10 (2)
H(7)	0.207 (7)	0.230 (2)	0.059 (6)	7 (1)
H(8)	0.323 (7)	0.233 (2)	0.335 (6)	7 (1)
H(15A)	0.53 (1)	0.168 (4)	0.74 (1)	22 (1)
H(15B)	0.457 (7)	0.161 (2)	0.929 (6)	6 (1)
H(15C)	0.568 (8)	0.107 (2)	0.881 (7)	8 (2)
H(16A)	−0.274 (8)	−0.007 (3)	0.516 (7)	8 (1)
H(16B)	−0.356 (7)	0.010 (2)	0.677 (6)	6 (1)
H(16C)	−0.22 (1)	−0.042 (4)	0.70 (1)	18 (1)
H(17A)	0.243 (8)	0.266 (2)	0.574 (6)	8 (1)
H(17B)	0.262 (7)	0.231 (2)	0.767 (5)	6 (1)
H(18A)	−0.439 (7)	0.130 (2)	0.350 (6)	8 (1)
H(18B)	−0.436 (8)	0.086 (2)	0.526 (6)	8 (1)

Table II. Carbon–Carbon Bond Distances and Carbon–Hydrogen Bond Distances for 2[a]

atom	atom	distance	atom	atom	distance
		Carbon–Carbon Bond Distances			
C1	C2	1.378 (7)	C7	C8	1.383 (8)
C1	C13	1.414 (7)	C8	C12	1.395 (7)
C1	C15	1.524 (8)	C9	C12	1.475 (7)
C2	C3	1.378 (8)	C9	C13	1.483 (7)
C3	C4	1.386 (8)	C9	C17	1.345 (7)
C4	C14	1.394 (7)	C10	C11	1.471 (7)
C4	C16	1.519 (8)	C10	C14	1.484 (6)
C5	C6	1.367 (8)	C10	C18	1.337 (7)
C5	C11	1.385 (7)	C11	C12	1.399 (6)
C6	C7	1.383 (8)	C13	C14	1.413 (6)
		Carbon–Hydrogen Bond Distances			
C2	H2	1.00 (5)	C15	H15C	0.92 (5)
C3	H3	0.88 (4)	C16	H16A	0.99 (5)
C5	H5	0.98 (5)	C16	H16B	0.93 (5)
C6	H6	1.07 (5)	C16	H16C	1.06 (9)
C7	H7	1.02 (5)	C17	H17A	1.08 (5)
C8	H8	1.01 (5)	C17	H17B	1.00 (4)
C15	H15A	1.2 (1)	C18	H18A	1.02 (5)
C15	H15B	0.97 (5)	C18	H18B	1.04 (5)

[a] All distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Two conformational energy minima were located for **2** by molecular mechanics procedures. The global minimum is a boat structure (ΔH_f = 69.7 kcal/mol, μ = 0.68 D) with a geometry nearly identical with that established by crystallography. In a comparison of the two structures, the root mean square deviation of all carbon atoms is 0.069 Å and for the central six-member ring plus exocyclic methylene carbons the value is only 0.022 Å. The second molecular mechanics minimum is a chair (ΔH_f = 75.5 kcal/mol, μ = 0.51 D), which suffers torsional and van der Waals strain in excess of that for the boat. Interestingly, we were unable to locate a minimum corresponding to a planar geometry. In contrast, for 9,10-anthraquinodimethane, Dewar[6b] has reported MNDO calculated minima for boat (ΔH_f = 85.1 kcal/mol) and planar geometries (enthalpy difference ca. 11 kcal/mol). For comparison, we

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(7) Dickerman, S. C.; Berg, J. H.; Haase, J. R.; Varma, R. *J. Am. Chem. Soc.* **1967**, *89*, 5457.

(8) Bowden, B. F.; Cameron, D. W. *Tetrahedron Lett.* **1977**, 383.

(9) For a detailed description of the preparation of **2** by the method of Bowden and Cameron,[8] see: Rosenfeld, S.; VanDyke, S. *J. Chem. Educ.* In press.

(10) A crystal structure determination for a carbamate derivative of 2-(hydroxymethyl)-11,11,12,12-tetracyanoanthraquinodimethane has been reported. Torres, E.: Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* **1987**, *52*, 2944.

(11) 1,4-Dimethyl-9,10-dihydro-9,10-bis(methylene)anthracene.

(12) The best available comparison to this structure is a tetracyanoanthraquinodimethane derivative that refined poorly and gave a value of 37.3° for the analogous angle.[10]

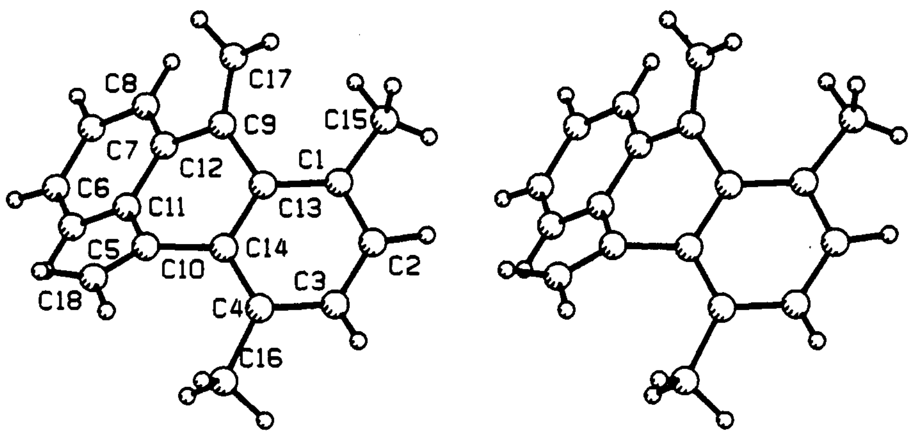

Figure 2. Stereo PLUTO[18] plot showing the molecular geometry and numbering scheme for 1,4-dimethyl-9,10-anthraquinodimethane (2).

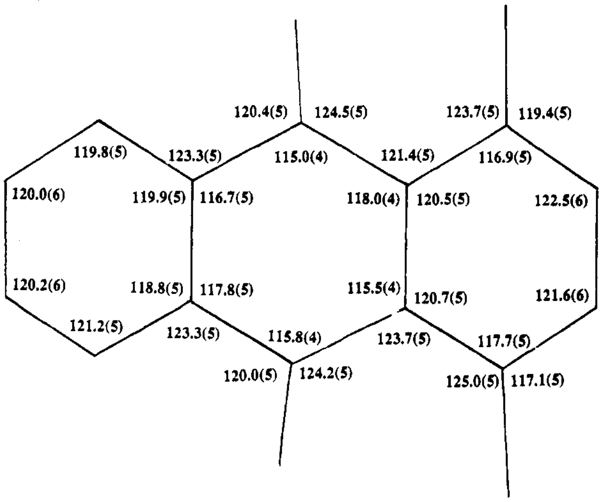

Figure 3. Carbon bond angles (deg) for 1,4-dimethyl-9,10-anthraquinodimethane (2) established by X-ray crystallography. Estimated standard deviations in the least significant figure are given in parentheses.

find boat (ΔH_f = 79.3 kcal/mol), planar (ΔH_f = 87.2 kcal/mol), and chair (ΔH_f = 84.1 kcal/mol) minima for that compound using molecular mechanics.

Experimental Section

The title compound was prepared from 1,4-dimethylanthraquinone as previously described.[8,9] Melting point, infrared spectra, and ^{1}H NMR spectra were as reported.[9] Crystallization of 2 from wet acetone yielded clear prism crystals of X-ray quality. Data collection for the X-ray structure analysis was done at ambient temperature on a crystal of approximate dimensions 0.4 × 0.2 × 0.7 mm. All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated molybdenum Kα radiation.[13] Twenty reflections were used for the unit cell determination (2θ range 20.1–26.9°, ω scan peak width at half-height 0.28), corresponding to a monoclinic cell in the space group $P2_1/a$ with the following lattice parameters: a = 6.760 (1) Å, b = 23.044 (5) Å, c = 8.454 (2) Å, β = 97.29 (1)°, V = 1306.2 (8) Å^3. For Z = 4 and formula weight 232.32, the calculated density was 1.181 g/cm^3. Of the 2574 reflections collected, 2371 were unique. The structure was solved by direct methods.[14,15] Neutral atom scattering factors were taken from Cromer and Waber.[16] Anomalous dispersion effects were included in F_{calc};[17] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[16]

All molecular mechanics calculations were done by using the MMX88 force field in the computer program PCMODEL, available from Serena Software, Bloomington, IN. MMX is a derivative of Allinger's MM2 with π VESCF subroutines. Structure comparisons were done by using the companion program PCDISPLAY, available from the same company.

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Supplementary Material Available: Additional tables of crystallographic data including torsion angles, bond angles involving the hydrogen atoms, and anisotropic thermal parameters for 2 (4 pages); table of observed and calculated structure factors for 2 (16 pages). Ordering information is given on any current masthead page.

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(13) Mo Kα (λ = 0.71069 Å), 6.0° take-off angle, ω-2θ scan, scan rate 8°/min, scan width (1.37 + 0.30 tan θ)°, $2\theta_{max}$ (50.5°), Lorentz-polarization and absorption corrections, secondary extinction (0.23589 × 10^{-5}).

(14) (a) Gilmore, C. J. MITHRIL, an integrated direct methods computer program. *J. Appl. Crystallogr.* 1984, *17*, 42. (b) Beurskens, P. T. "DIRDIF: Direct Methods for Difference Structures-An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors"; Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegan, The Netherlands.

(15) All calculations were performed by using the TEXSAN, TEXRAY Structure Analysis Package, version 2.1, of Molecular Structure Corporation, The Woodlands, TX. Full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$, $4F_o^2/\sigma^2(F_o^2)$, p factor (0.03), 997 observations ($I > 3.00\sigma(I)$), 228 variables, reflection/parameter ratio (4.37), R = 0.058, R_w = 0.076, goodness of fit 2.47, maximum shift/error in final cycle (0.08), maximum peak in final difference map (0.20 e$^-$/Å^3), minimum peak in final difference map (−0.17 e$^-$/Å^3).

(16) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Vol IV; The Kynoch Press: Birmingham, England, 1974; Tables 2.3.1 and 2.2A.

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Diels–Alder Reactions of N-Sulfonyl-1-aza-1,3-butadienes: Development of a Synthetic Approach to the Streptonigrone C Ring

Dale L. Boger* and Shinsuke Nakahara

Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907

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Streptonigrone (1), isolated from an unidentified *Streptomyces* species and identified through extensive

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