(*pace* Nelson and Hintz[3] the dipole moments are reproducible and are not due to impurities) and also with Raman and infrared evidence as will be discussed in our full paper.

(7) On sabbatical leave (1972–1973) from the College of Pharmacy, Washington State University, Pullman, Wash.

(8) On sabbatical leave (1969–1970) from the Department of Chemistry, Concordia College, Moorhead, Minn.

(9) On sabbatical leave (1972–1973) from the Department of Chemistry, Eastern Michigan University, Ypsilanti, Mich.

R. A. Y. Jones, A. R. Katritzky,* A. R. Martin[7]
D. L. Ostercamp,[8] A. C. Richards, J. M. Sullivan[9]

School of Chemical Sciences, University of East Anglia
Norwich, England

X-Ray Crystal Structure of a Diaryldialkoxysulfurane Oxide[1]

Sir:

We report the results of a single-crystal X-ray structure determination on the recently described[2] sulfurane oxide **1**.[3] This is the first X-ray structural study re-

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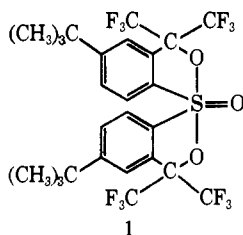
ported for a pentacoordinate sulfur(VI) compound. The nonequivalence of the trifluoromethyl groups,[2] which is evidenced in the ^{19}F nmr spectrum of **1**, is consistent with most of the structural models which have been considered for such species, including the trigonal bipyramidal model and the tetragonal pyramidal model. The present study establishes an approximate trigonal bipyramidal geometry about sulfur with the electronegative alkoxy groups occupying apical positions and with the two aryl groups and the oxide oxygen occupying equatorial positions.

Sulfurane oxide **1** was recrystallized several times from petroleum ether and a single crystal was selected and mounted in the usual way: $C_{26}H_{24}F_{12}O_3S$, M = 644.5; monoclinic; $a = 13.824$ (9), $b = 12.231$ (5), $c = 20.846$ (11) Å; $\beta = 126°55'$ (1'); $V = 2818$ Å^3; $Z = 4$; $\rho_{calcd} = 1.52$ g cm^{-3}; $F(000) = 1312$; space group $P2_1/c$ from systematic absences, $h0l$, when $l = 2n + 1$, $0k0$, when $k = 2n + 1$; nickel filtered Cu $K\alpha$ X-radiation; λ 1.54178 Å; $\mu(Cu\ K\alpha) = 20.3$ cm^{-1}.

A single crystal was used to obtain the intensity data on a Picker FACS-1 diffractometer. A total of 3005 nonzero reflections was obtained using Cu $K\alpha$ radiation. The structure was solved by the symbolic addition procedure,[4] using the FAME–SYMPL–MAGIC

(1) Paper number XI in a series on sulfuranes. For paper X in this series see J. A. Franz and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 2017 (1973).

(2) E. F. Perozzi and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5519 (1972).

(3) For other examples of pentacoordinate sulfur(VI) species containing halogen ligands, see (a) S. P. von Halasz and O. Glemser, *Chem. Ber.*, **103**, 594 (1970); (b) S. P. von Halasz, O. Glemser, and M. F. Feser, *ibid.*, **104**, 1242 (1971); (c) J. M. Shreeve, *Accounts Chem. Res.*, **6**, 387 (1973).

(4) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

series of programs,[5] and refined initially by Fourier methods. At the present stage of refinement[6] (hydrogen atoms located and anisotropic thermal parameters for the nonhydrogen atoms) the crystallographic R factor on all nonzero reflections is 0.072. Some ambiguity is evident in the location of the hydrogen atoms on the *tert*-butyl groups, indicating the possibility of disorder of these hydrogens due to rotation of 60° about the C–CH$_3$ bonds. A stereoscopic view of the structure is shown in Figure 1.

The only other pentacoordinate sulfur(VI) compound for which structural data are available is sulfur oxytetrafluoride, OSF$_4$. Electron diffraction studies on this compound have resulted in the proposal of various models to account for the data. The models[7–9] are in agreement as to the overall trigonal bipyramidal geometry of the molecule, but there is some uncertainty as to the finer structural details. The internal equatorial F–S–F angle has been reported as 122.8 (1.8)°,[7] 110.01 (74)°,[8] and 110.1 (1.8)°,[9] while the axial F–S–F angle has been reported as 182.8 (7)°,[7] 178.35 (48)°,[8] and 178.8 (4)°.[9] In the first model,[7] the axial F–S–F angle is bent *in* the direction of the equatorial oxygen, *away* from the equatorial fluorines, while in the two more recent models[8,9] the direction of distortion from linearity is *away* from the equatorial oxygen. The structure determination of **1**, showing the O–S–O (axial) angle to be 172.3 (2)° and the distortion from linearity *away* from the equatorial oxygen, supports the more recently proposed structures for OSF$_4$.[8,9]

The C–S–C angle of **1** (117.7 (3)°) is considerably larger than the C–S–C angle of dialkoxydiarylsulfurane, **2** (104.4 (3)°),[10] or of the spirodiaryldiacyloxysulfurane, **3** (107.8 (8)°).[11] The distortion of the trigonal

2   3
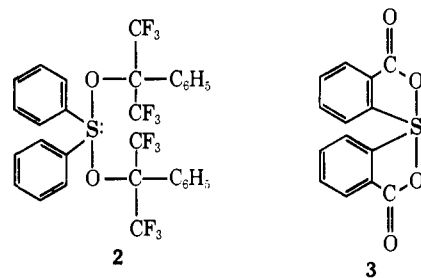
bipyramid which reduces the C–S–C angles of **2** and **3** below 120° has been interpreted[10] as a reflection of the 3s–3p energy level separation, which causes the lone pair of electrons to utilize more of the s character[12] while the S–C bonds tend to acquire more p character. In sulfurane oxide **1** there is no lone pair, hence one would expect the equatorial angles to approach the 120° value appropriate to sp^2 hybridization, as is observed.

(5) (a) E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, Abstracts, American Crystallographic Association, Atlanta, Ga., Jan 1967, Paper A7, p 20; (b) R. B. K. Dewar, Ph.D. Thesis, University of Chicago, 1968.

(6) See paragraph at end of paper regarding supplementary material.

(7) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963).

(8) J. L. Hencher, D. W. J. Cruickshank, and S. H. Bauer, *J. Chem. Phys.*, **48**, 518 (1968).

(9) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969).

(10) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Amer. Chem. Soc.*, **94**, 5010 (1972); **93**, 6674 (1971).

(11) (a) A. Kálmán, K. Sasvári, and I. Kapovits, *Acta Crystallogr.*, *Sect. B*, **29**, 355 (1973); (b) I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).

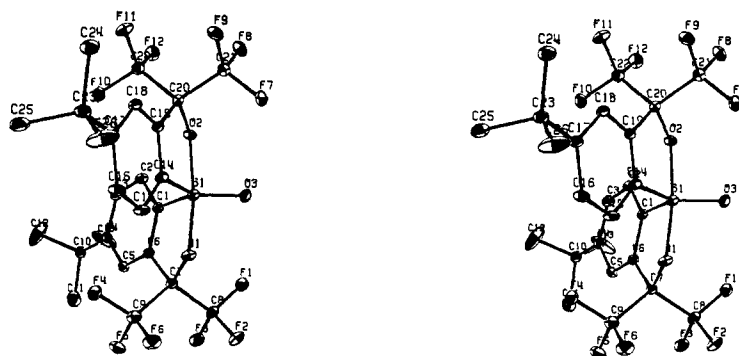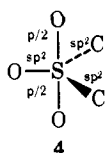(12) See, for example, H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

Figure 1. Stereoscopic drawing of **1**. Hydrogen atoms were not included in the drawing. The S–O(axial) lengths are 1.780 (5) and 1.777 (5) Å; the S–O(equatorial) bond length is 1.439 (4) Å, and the S–C lengths are 1.784 (5) and 1.796 (6) Å. The O–S–O(axial) angle is 172.3 (2)°; the C–S–C angle is 117.7 (3)°; the C–S–O (axial oxygen) angles range from 87.4 (2) to 94.3 (2)°; and the C–S–O (equatorial oxygen) angles are 120.7 (2) and 121.5 (3)°.

The S–O bond lengths in **1** of 1.780 (5) and 1.777 (5) Å are shorter than those of sulfurane **2** (1.889 (4) and 1.916 (4) Å),[10] those of spirosulfurane **3** (1.83 (1) Å),[11] or those of a related sulfurane.[13] They also represent the shortest S–O distances among sulfur compounds that have nearly linear X–S–O geometry (X = N, S, or O).[14] The lengthening of the S–O bond in **2** over the covalent radii sum of 1.70 Å[15] has been explained[10] in terms of hypervalent bonding theory[16,17] in which two electrons are placed in the three-center (O–S–O) bonding molecular orbital (giving a bond order of 0.5 for the two S–O bonds) and two into the nonbonding orbital (putting negative charge on the electronegative apical substituents). A similar picture (**4**) can be adopted here in which the apical bonds are

$$
\begin{array}{c}
\text{O} \\
\text{p/2}\,|\quad\;\text{sp}^2\text{C} \\
\text{O}\overset{\text{sp}^2}{-}\text{S}\overset{\text{sp}^2}{\diagdown} \\
\text{p/2}\,|\quad\;\text{C} \\
\text{O}
\end{array}
$$

4

described as (p/2) hybridized while the equatorial bonds are sp² hybridized.

This picture of bonding in sulfuranes, which invokes no d orbital or higher s orbital character in the three-center four-electron apical bonds to sulfur, has been elaborated in earlier publications.[10,16–18] The equatorial S–O bond in **1** (1.439 (4) Å) is slightly longer than that reported for OSF₄ (1.422 (8),[7] 1.413 (1),[8] or 1.403 (3)[9] Å) but is, however, considerably shorter than the S–O bond lengths found in sulfoxides, for

example, diphenyl sulfoxide (1.473 (16) Å),[19] cis-9-methylthioxanthene 10-oxide (1.492 (3) Å),[20] trans-thioxanthen-9-ol 10-oxide (1.484 (8) Å),[21] and β-thianthrene dioxide (1.479 (16) and 1.474 (16) Å).[22] It is close in length to the S–O bond lengths in bis(p-chlorophenyl)sulfone (1.432 (5) Å),[23] bis(p-amino-phenyl) sulfone (1.44 and 1.45 Å),[24,25] bis(p-iodophenyl) sulfone (1.43 Å),[26] and dimesityl sulfone (1.413 (10) and 1.410 (6) Å).[27]

The similarity of the S–O bond length in **1** to the sulfone S–O bond lengths may reflect pπ–dπ bonding between sulfur and oxygen similar to that usually invoked[28] for sulfones. On the other hand, the change in hybridization in the σ bond from sulfur to oxygen from ca. sp³ in the sulfone to ca. sp² in **1** might have been expected[29] to result in some bond shortening. Chemical evidence for a greater resemblance to sulfones than to sulfoxides will be presented in a later publication. The detailed comparison of bond lengths and angles of **1** with those of its precursor spirosulfurane[13] will also be the subject of a later paper.

(13) The X-ray crystal structure of the spirodialkoxydiarylsulfurane precursor to **1** (the molecule lacking the equatorial oxygen of **1**)² is being determined and has been refined in its preliminary stages to an R value of 0.094. In this sulfurane the apical S–O bond lengths for two independent molecules of the refinement are 1.832 (5), 1.819 (5), 1.831 (5), and 1.816 (5) Å, shorter than those of **2** and about the same as those of **3**.

(14) (a) E. C. Llaguno and I. C. Paul, *Tetrahedron Lett.*, 1565 (1973); (b) P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc. B*, 946 (1971).

(15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 221–228.

(16) R. E. Rundle, *Surv. Progr. Chem.*, **1**, 81 (1963).

(17) (a) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); (b) J. I. Musher, in "Sulfur Research Trends," D. J. Miller and T. K. Wiewiorowski, Ed., American Chemical Society, Washington, D. C., 1972, Chapter 3.

(18) See, however, L. J. Kaplan and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 793 (1973), for experimental support for the possibility that charge distribution may be affected by contributions of these higher energy atomic orbitals of sulfur to this molecular orbital.

(19) S. C. Abrahams, *Acta Crystallogr.*, **10**, 417 (1957).

(20) J. Jackobs and M. Sundaralingam, *Acta Crystallogr., Sect. B*, **25**, 2487 (1969).

(21) A. L. Ternay, Jr., D. W. Chasar, and M. Sax, *J. Org. Chem.*, **32**, 2465 (1967).

(22) S. Hosoya, *Acta Crystallogr.*, **21**, 21 (1966).

(23) J. G. Sime and S. C. Abrahams, *Acta Crystallogr.*, **13**, 1 (1960).

(24) C. Dickinson, J. M. Stewart, and H. L. Ammon, *Chem. Commun.* 920 (1970).

(25) Similar values may be calculated from the data of M. Alleaume and J. Decap, *C. R. Acad. Sci.*, **261**, 1693 (1965).

(26) C. Keil and K. Plieth, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **106**, 388 (1955).

(27) S. A. Chawdhury and A. Hargreaves, *Acta Crystallogr., Sect. B*, **27**, 548 (1971).

(28) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); J. R. VanWazer and I. Absar in "Sulfur Research Trends," D. J. Miller and T. K. Wiewiorowski, Ed., American Chemical Society, Washington, D. C., 1972, Chapter 2.

(29) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 150.

Edmund F. Perozzi, J. C. Martin,* Iain C. Paul*

*The School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801*

Received September 15, 1973

Structure and Stereochemistry of Cyclobutatusin, a Diterpenoid Containing a Four-Membered Ring

Sir:

Biological screening of plants from Brazilian flora[1] led to an investigation of the bitter principles contained in the leaves of *Coleus barbathus* (*Labiatae*) which are currently used in popular medicine as a stomach aid.[2] This study has resulted in the isolation and characterization of barbatusin (Ia), a diterpene containing a spirocyclopropane ring attached at C-13.[3] We wish to report now the structures of two of the minor constituents identified in this plant. The more interesting compound is cyclobutatusin (IIa), a novel diterpenoid which retains the basic ring skeleton of barbatusin, but has the outstanding new feature of a four-membered ring formed by a bond between C-1 and C-11.

Ia, R = O

b, R = <OH / H

IIa, R = H

b, R = COC₆H₄Br
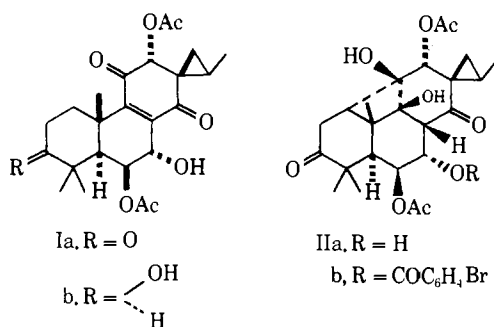
Chromatography on silica gel of an acetone extract of the plant material afforded, upon elution with an acetone–chloroform mixture, cyclobutatusin (0.008%), mp 196–200°, $C_{24}H_{32}O_9$ (M⁺ 464). No major uv absorption maximum above 210 nm was observed, whereas the ir spectrum (KBr) indicated the presence of hydroxyl, keto, and ester functions (3600, 1710, 1380, 1200 cm⁻¹). The nmr spectrum ($CDCl_3$, ppm) indicated three tertiary and one secondary C-methyl group signals (s at 1.12, 1.13, and 1.34; d at 1.19, J = 6.5 Hz) for the 18-, 19-, 20-, and 17-CH₃, respectively; two acetyl functions at 2.02 (3 H, s, 6β-OAc) and 2.11 (3 H, s, 12α-OAc), two CHOAc protons at 5.54 (d of d, $J_{5,6}$ = 4.8 and $J_{6,7}$ = 6.4 Hz) and at 5.58 (s) for the 6α-H and 12β-H; the complex signal pattern of the three hydroxyl groups (br signals at 4.3 and 4.49 with $W_{1/2}$ = 22 and 14 Hz) collapsed following deuterium exchange (with D_2O) into a simple d of d at 3.97 ppm ($J_{6,7}$ = 6.4 and $J_{7,8}$ = 4 Hz, assigned to the 7β-H). Cyclobutatusin readily formed a mono-*p*-bromobenzoyl

(1) C. M. Rosito, D. Erlich, M. Nakagawa, and R. Zelnik, *An. Acad. Brasil. Cienc.*, **43**, 687 (1971).

(2) A preliminary antitumor screening of an extract of the leaves has shown no significant activity against L-1210 lymphoid leukemia in mice. The tests were performed under the auspices of the Cancer Chemotherapy National Screening Center, National Cancer Institute.

(3) A. H.-J. Wang, I. C. Paul, R. Zelnik, K. Mizuta, and D. Lavie, *J. Amer. Chem. Soc.*, **95**, 598 (1973).

ester (IIb), $C_{31}H_{35}O_{10}Br$, mp 286–288° (M⁺ 646 and 648), a fact which pointed out that two of the hydroxyl groups were tertiary. From the detailed spectroscopic analyses and from biogenetic considerations, a structure related to barbatusin (Ia) was strongly suggested for cyclobutatusin. At this stage, recourse was made to X-ray analysis for determination of the structure.

A colorless rectangular plate-shaped crystal of the *p*-bromobenzoyl ester (IIb) obtained by crystallization from benzene was used to deduce the structure and stereochemistry of cyclobutatusin by X-ray analysis. Crystal data are: $C_{31}H_{35}O_{10}Br$; mol wt 647.5; orthorhombic; a = 14.091 (3), b = 15.268 (3), c = 14.018 (3) Å; V = 3016 Å³; ρ_{obsd} = 1.44 g cm⁻³; Z = 4; ρ_{calcd} = 1.43 g cm⁻³; $F(000)$ = 1344; μ (Cu Kα) = 25.6 cm⁻¹; space group $P2_12_12_1$. A total of 2241 nonzero reflections out to 2θ = 130° was measured on a Picker FACS-1 diffractometer using Cu Kα radiation.[4] The structure was solved by the heavy atom method and refined by full-matrix least-squares methods with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were located at the most probable positions based on two successive difference maps and were included in the structure factor calculations but were not refined. The absolute configuration of II was assumed to be related to that of barbatusin. The final R factor was 0.069. A stereoscopic drawing of the molecule of IIb is shown in Figure 1.

The striking geometrical features of the molecule are the highly constrained skeleton and the overall compactness. If one neglects the *p*-bromobenzoyl side group, the molecule IIb assumes a bowl shape with the two adjacent hydroxyl groups at C-9 and C-11 exposed on the surface of the bottom of the bowl. The cyclobutane ring is not planar but has a dihedral angle of 19.0° between the planes defined by C-11, C-1, and C-10 and by C-11, C-9, and C-10.

During the chromatographic fractionations, a second minor compound was isolated and was assigned the structure Ib (3β-hydroxy-3-deoxobarbatusin (0.014%)) on the following grounds: $C_{24}H_{32}O_8$ (M⁺ 448); uv max (EtOH) 235 nm (ε 18,273); ir (KBr) 3600, 1730, 1700, 1680, 1604, 1370, 1230 cm⁻¹. The nmr spectrum ($CDCl_3$, ppm) was particularly informative in that it revealed the presence of three tertiary C-methyl groups, signals at 0.99 (3 H, s, 18-CH₃),[5] 1.14 (3 H, s, 19-CH₃), and 1.66 (3 H, s, 20-CH₃), a secondary C-methyl group at 1.1 (3 H, d, $J_{15,17}$ = 6.5 Hz, 17-CH₃), two acetyl functions at 2.02 (3 H, s, 6β-OAc), 2.06 (3 H, s, 12α-OAc), two hydroxyl groups, broad signal centered at 2.80 (2 H, $W_{1/2}$ = 22 Hz, 3β- and 7α-OH), one proton at 3.28 (d of d, $J_{3,2}$ = 7.0 and 9.0 Hz for 3α-H),[6] one

(4) During the course of data collection (~8 days), the intensities of the three standards fell off gradually and the orientation matrix had to be recalculated several times. At the end of data collection the standards had fallen to 83% of their initial values and the cell dimensions were remeasured and found to be a = 14.141 (5), b = 15.250 (6), and c = 14.075 (5) Å. These differences suggested that in a few of the unit cells the compound may have undergone some change under X-ray irradiation. However, no clear evidence to indicate the nature of this change could be obtained from our X-ray study. A linear scale factor was applied to correct the fall-off in the intensities.

(5) The numbering system used in the discussion of the nmr spectra of Ib is that of the abietane ring system, which differs somewhat from that used to describe the molecular geometry of IIb (Figure 1).

(6) The β (equatorial) configuration of the hydroxyl group was established on the basis of the coupling constants of the methine proton at C-3. The latter proton is shown to be axially oriented on the basis of the angle values derived from the Karplus equation.