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SYNTHESIS, STRUCTURAL ELUCIDATION AND STEREOCHEMISTRY OF FIVE-COORDINATE ORGANOARSENIC CATECHOLATES

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April 1982

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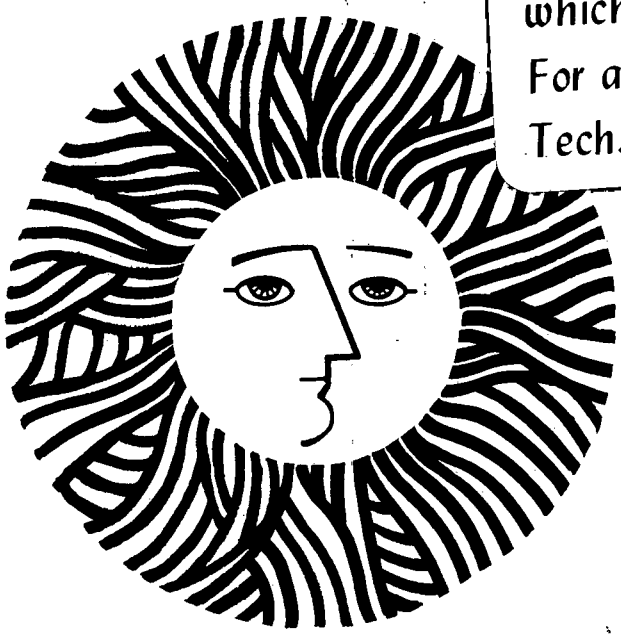

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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This work was supported by the Assistant Secretaries for Fossil Energy and Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center Of the U.S. Department of Energy under Contract number DE-AC03-76SF00096.

Abstract

The reactions of methyl and phenylarsonic acids with substituted catechols was studied. These reactions produced five-coordinate organoarsenic catecholates, which were characterized by 250MHz ^{1}H NMR spectroscopy, IR spectroscopy, EI mass spectrometry and elemental analyses. The possibility of cis and trans isomers for several of the substituted catecholate organoarsenic compounds was verified by NMR spectroscopy, and in one case, single crystal x-ray crystallography.

This latter x-ray study provided, for the first time, unequivocal evidence for cis stereochemistry of methyl groups attached to the catecholate rings, a retangular pyramidal configuration (95%) of the oxygen atoms surrounding the arsenic atom with a phenyl group in the axial position.

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Summary: The synthesis of five-coordinate organoarsenic catecholates, with substitution of 3-CH_3-; 4-$CH_3OC(=O)$-; 4,5- , and 3,3'-$C(=O)N(H)(CH_2)_4NC(=O)$- groups on the catechol ring and CH_3 or Ph on arsenic, was performed. These reactions provided new insights into the structures and stereochemistry of these organoarsenic compounds. In one case, 3-methylcatecholate of phenylarsonic acid, a single crystal x-ray analysis provided unequivocal evidence for cis stereochemistry of the methyl groups on the catechol rings, an essentially rectangular pyramidal configuration around arsenic, and a prefered conformation of the phenyl group in relation to the oxygens surrounding the arsenic atom.

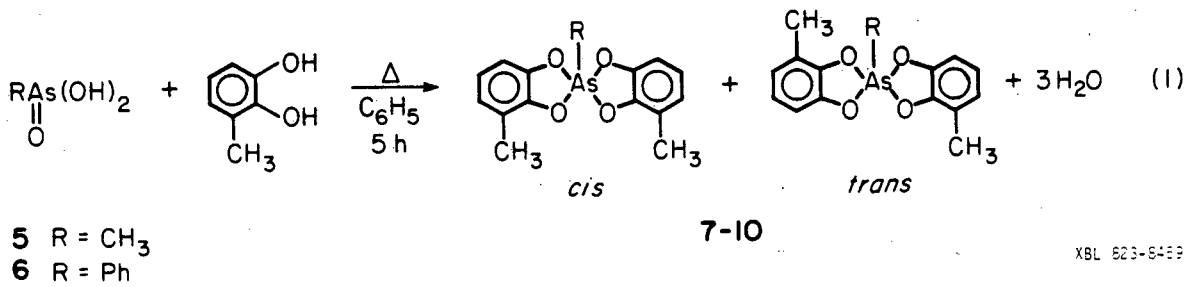
Recently, we have been investigating the speciation or molecular characterization of organoarsenic compounds thought to present in biogeochemical materials such as oil shale kerogen and the products of the pyrolysis of oil shale kerogen, those of the shale oils and the retort waters[1a,b]. These studies led to the identification, for the first time, of methyl and phenylarsonic acids in these precursors and products.

In view of these discoveries, we have initiated studies to find innovative methods for the removal of these compounds and other organometallics from fossil fuel products. In this regard, we have been experimenting with a method that utilizes substituted catechols as

potential ligands that could be placed in a polymeric matrix for the future removal of organoarsenic compounds from the above mentioned products.

Surprisingly, we found very few references on the reactions of catechols with alkyl or arylarsonic acids[2a-c] and none on similar reactions with substituted catechols[3]. Thus, in this communication, we present our initial results on the synthesis, structural elucidation and stereochemistry of the five-coordinate organoarsenic catecholates we prepared as model compounds for the above mentioned purposes.

Chart 1 shows the catechols, 1-4, we utilized in the reactions with methyl or phenylarsonic acid, 5 and 6. Compound 1 reacts with either 5 or 6 to provide a mixture of cis and trans five-coordinate organoarsenic catecholates, 7 - 10 (Eq. 1).



Compounds 7-10 were characterized by a combination of nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS), infrared spectroscopy (IR) and elemental analysis.[4] The 250 MHz NMR spectrum provided definitive evidence that compound 1 reacted with either 5 or 6 to give a mixture of cis and trans isomers (7, 8 R= CH_3 and 9, 10 R = Ph). Thus, compounds 7 and 8 showed two methyl resonances (catecholate ring) at 2.21 and 2.19 ppm (benzene-d_6, TMS) and two methyl resonances for

groups bonded to arsenic at 1.33 and 1.32 ppm in the ratio of 53:47. The corresponding cis and trans compounds, 9 and 10, where R=Ph, had methyl resonances at 2.26 and 2.12 ppm (benzene-d_6, TMS) in the ratio of 90:10. The complexity of the phenyl region at 250 MHz did not allow a separation of catecholate protons and phenylarsenic protons and thus the ^{1}H NMR spectrum was obtained at 400 MHz. The ^{1}H 400 MHz NMR spectrum of 9, 10 (benzene-d_6, TMS) showed resonances at 7.81 (doublet, J=8.3Hz); 6.83 (multiplet) and 6.74 ppm (overlapping triplets J=8.3Hz) for the phenylarsenic protons in the ratio of 2:1:2. The catecholate protons were found at 6.56 (doublet of doublets, J_{ortho}=7.8 Hz, J_{meta}=1.4 Hz); 6.65 (overlapping triplets, J=7.8 Hz), 6.93 (triplet, J=7.8 Hz) and 2.24 ppm (singlet) in the ratio of 2:2:2:3. The complexity of the phenyl region, where protons on the phenyl group attached to arsenic appeared to be all non-equivalent, provided tentative evidence for the cis isomer, 9, rather than the trans isomer, 10, as the major product in this reaction.

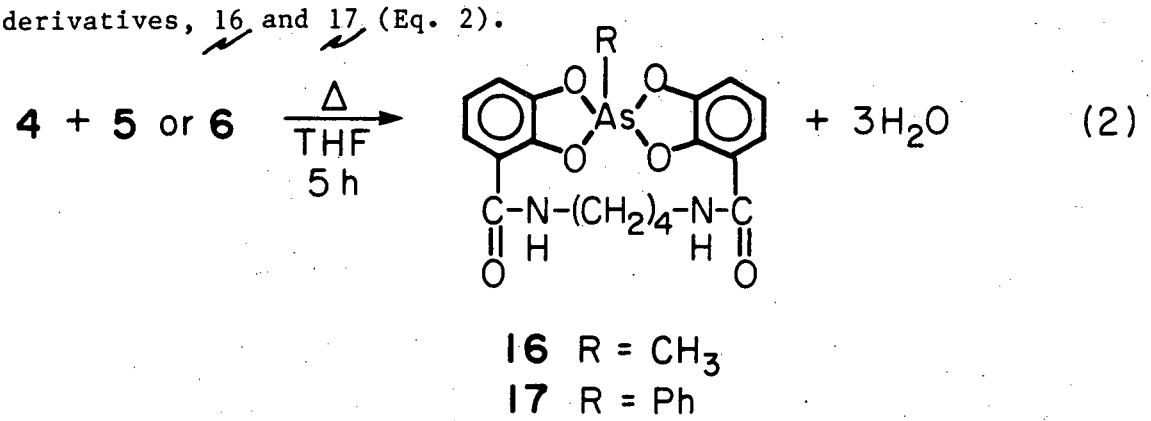
In order to unequivocally ascertain the stereochemistry of the major isomer, either 9 (cis) or 10 (trans), we obtained a single-crystal x-ray analysis.[5] Figure 1 shows the ORTEP drawing of the major isomer, 9, with the methyl groups clearly cis to each other and the geometry around the arsenic, essentially rectangular pyramidal(95%), while the axial phenyl group is twisted so that it lies in the same plane as oxygen 2 and oxygen 3. The angle between the carbons 1 and 6 on the phenyl group attached to arsenic and the oxygen-arsenic-oxygen plane is 4.7°. This represents the first rectangular pyramidal and stereochemical assignment that has been made for a five-coordinate organoarsenic

catecholate with substitution on the catecholate rings (see Table 1 for pertinent bond lengths and angles).[6]

Compound 2 reacted with 5 to provide a compound, 11, with a single methylarsenic resonance at 1.92 ppm (^{1}H, 250MHz, DMSO-d_6, TMS) and a single methoxyl resonance at 3.78 ppm and is indicative of one isomer, which we presume to have cis stereochemistry as in 9. Compound 2 also reacts with 6 to provide a mixture of compounds, 12 and 13, with two methoxyl signals (^{1}H, 250 MHz, DMSO-d_6, TMS) at 3.76 and 3.74 ppm in the ratio of 95:5. Again, as with 11, we presume cis stereochemistry for the major isomer. Compound 3, a benzo-substituted catechol, reacted with 5 or with 6 to give the five-coordinate organoarsenic compounds 14 and 15 respectively. While no stereochemistry is involved in the formation of either 14 or 15, it is important to note that substitution on the naphthyl ring is certainly possible for future attachment of this type of compound to a polymeric backbone. The pertinent NMR data (^{1}H 250 MHz, DMSO-d_6, TMS) provided an upfield shift, as with the NMR spectra of compounds 7-13, for the catechol ring protons of 14 and 15 when compared to 3. Thus, 14 had the catechol protons (singlet) at 7.09 ppm, 15 at 7.10 and 3 at 7.12 ppm indicative of the arsenic atoms influence on shifting, to higher fields, protrons on catechol rings. A similar NMR result was obtained by Raymond et al.[7] for some gallium and rhodium catecholate complexes.

Our final ligand of interest, 4[8], was important to study, since it represented a model for a recently reported polymer of potential use for our future applications[9]. We chose 4 (4-LICAM) after making Dreiding models that clearly showed the central cavity being able to accomodate

an arsenic atom (~3.58 to 3.63 A, see Figure 1). Reaction of 4, with either 5 or 6, provided the intramolecular five-coordinate organoarsenic derivatives, 16 and 17 (Eq. 2).



(2)

The ^1H 250 MHz NMR and 70 ev MS (solid probe) data were consistent with the structures assigned. Notably, the mass spectra provided the parent ion and an ion resulting from a loss of the catechol group with a carbonyl attached. This was followed by a fragmentation of the $-CH_2CH_2-NH$ groupings. For example, with 17 the MS ions of interest were: m/e 508 ($M^{+\cdot}$); 373 ($M-C_7H_{13}N_2O_3$) 331 ($M-C_9H_8NO_3$); and 287 ($M-C_{11}H_{13}N_2O_3$).

A typical procedure for the preparation of a five-coordinate organoarsenic catecholate derivative is described as follows for 9.

In a 50 ml flask, equipped with condenser and drying tube, was placed 1.29g (10.42 mmole) of phenylarsonic acid and 1.05 g (5.21 mmole) 3-methylcatechol (freshly sublimed) in 30 ml of benzene. The reaction mixture was refluxed for 5h. The benzene was removed on a rotary evaporater and the compound recrystallized from carbon tetrachloride/methanol and dried under vacuum to give 1.88g (91% yield) of 9, mp, 134-135°C. Calculated for $C_{20}H_{17}O_4As$; C, 60.6; H, 4.3, Found: C, 60.39; H, 4.46; EIMS (70 ev, solid probe) m/e 396 ($M^{+\cdot}$), 274, 197,

151, 106.[10]

In future experiments, we hope to place several of our catechol derivatives in polymeric backbones to see if their reactivity remains in reactions with organoarsonic acids.

Acknowledgements

We wish to thank Drs. F. L. Weitl and K. N. Raymond for several samples of LICAM derivatives for evaluation and helpful suggestions during the initial stages of this project. Helpful discussions with Drs. K. Irgolic and R. Zingaro are also acknowledged. We wish to thank Drs. F.E. Brinckman and R.B. Johannesen, of the National Bureau of Standards, for obtaining the 400 MHz ^{1}H NMR spectrum of 9. The crystal structure analysis for 9 was performed by Dr. F.J. Hollander at U.C. Berkeley x-ray Crystallographic Facility (CHEXRAY). The work was supported by the Assistant Secretaries for Fossil Energy and Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center (project manager, Dexter Sutterfield) of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

Supplementary Material Available

A listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(1) a) Fish R.H., Brinckman F.E. and Jewett K.L., Environ. Sci. Technol., 1982, 16, 174.

b) Weiss C.S., Brinckman F.E. and Fish R.H., Proceedings on

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(2) a) Salmi E.J., Merivuori K. and Laaksonen E., Kemistilehti Suomen 1946, 19B, 102, (CA, 41, 5440a).

b) Bacher J.H. and Van Oosten R.P., Rec. Trav. Chem. 1940, 59, 41.

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(3) Fish R.H. and Weitl F.L., Xth International Conference on Organometallic Chemistry, Toronto, Canada, August 9-14, 1981, Abstract 1D12, p. 62.

(4) All new compounds we report had elemental analyses (C, H, N) within ± 0.5% of theory. The EIMS, IR and NMR spectra for all compounds supported their structures.

(5) Crystal data for 9: space group $P\bar{1}$, a=9.3734(8)Å, b=9.3823(12)Å, c=11.3718(15)Å, α=69.433(10)°, β=70.809(9)°, γ=72.631(8)°, V=865.7(2)A^{o3}, formula weight: 396.28 amu, Z = 2, d = 1.52g/cm^3, μ=19.76 cm^1, size: 0.21 x 0.33 x 0.37 mm. The structure was solved by Patterson and Fourier Techniques and refined via normal least squares procedures: R=3.47% and Rw=5.49% using 2242 reflections with F^2>3 F^2. The crystals of 9 were grown in a solvent mixture of carbon disulfide and pentane (1:1) by slow evaporation.

(6) Several other x-ray studies on five-coordinate organoarsenic glycolate and catecholate derivatives have been done. However, in both cases a distorted retangular pyramidal configuration around arsenic (60-75% RP) was found and no stereochemical characteriza-

tion was attempted, i.e., substituted catechols were not used. (See Goldwhite H. and Teller R.G. , J. Am. Chem. Soc. 1978, 100, 5357. Wunderlich, H. Acta Cryst. 1978, B34, 1000.)

See Holmes, R.R. and Deiters, J. J. Am. Chem. Soc. 1977, 99, 3318 for idealized angles for square pyramidal, retangular pyramidal and trigonal bipyramidal structures and methods of analysis. Using the angle deviation analysis method of Holmes and Deiter, we find a minimum deviation sum for the rectangular pyramidal structure of 11.2^{o} (~95% distortion from trigonal bipyramidal toward rectangular pyramidal) for compound 9.

(7) Mcardle J.V., Sofen S.R., Cooper S.R., and Raymond K.N., Inorg. Chem. 1978, 17, 3075.

(8) The series of LICAM derivatives of increasing methylene chain, 2-6, were prepared according to the procedures of Dr. F.L. Weitl (cf. F.L. Weitl and K.N. Raymond, J.Amer. Chem. Soc. 1980, 102, 2289).

(9) Dawson M. I., Chan R.L.-S., Cloudsdale I.S. and Harris W.R., Tetrahedron Letters, 1981, 22, 2739.

(10) We have used this procedure to derivatize phenylarsonic acid, 6, that had been isolated from a Green River oil shale kerogen by extraction with methanol. Since 9 can be chromatographed on a 30 m fused silica capillary column (OV101), the use of GC-MS will enhance the utility of these organoarsonic acid derivatives for other applications. Fish, R.H., Tannous, R.S., Weiss, C.S., and Brinckman, F.E., in preparation.

Table I

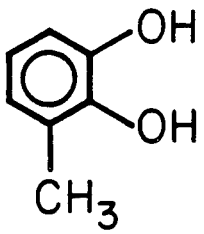
Selected Bond Lengths and Angles for
cis $(3\text{-}CH_3\text{-}C_6H_3O_2)_2AsC_6H_5$, 9[a]

Atoms	Bond length Å	Atoms	Angle, Deg
$As\text{-}O_1$	1.806 (.001)	$O_1\text{-}As\text{-}O_2$	87.93 (.07)
$As\text{-}O_2$	1.799 (.002)	$O_1\text{-}As\text{-}O_3$	85.43 (.07)
$As\text{-}O_3$	1.784 (.002)	$O_1\text{-}As\text{-}O_4$	150.84 (.09)
$As\text{-}O_4$	1.825 (.002)	$O_2\text{-}As\text{-}O_3$	149.85 (.09)
$As\text{-}C_1$	1.899 (.002)	$O_2\text{-}As\text{-}O_4$	82.71 (.08)
$C_7\text{-}O_1$	1.365 (.003)	$O_3\text{-}As\text{-}O_4$	88.95 (.09)
$C_8\text{-}O_2$	1.370 (.003)	$O_1\text{-}As\text{-}C_1$	105.5 (.08)
$C_{14}\text{-}O_3$	1.413 (.003)	$O_2\text{-}As\text{-}C_1$	104.99 (.09)
$C_{15}\text{-}O_4$	1.345 (.003)	$O_3\text{-}As\text{-}C_1$	105.12 (.09)
$C_{12}\text{-}C_{13}$	1.474 (.004)	$O_4\text{-}As\text{-}C_1$	103.59 (.09)

[a]Estimated standard deviations in parenthesis

Figure 1. ORTEP diagram of <u>cis</u> $(3\text{-}CH_3\text{-}C_6H_3O_2)_2AsC_6H_5$, 9, showing 20% probability ellipsoids.

Chart I. Catechols used in the synthesis of five coordinate organoarsenic catecholates



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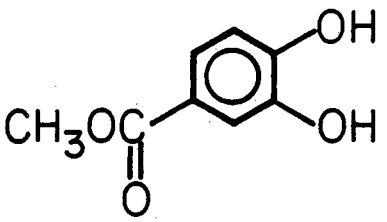

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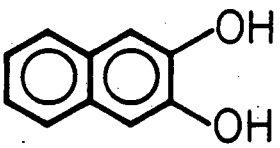

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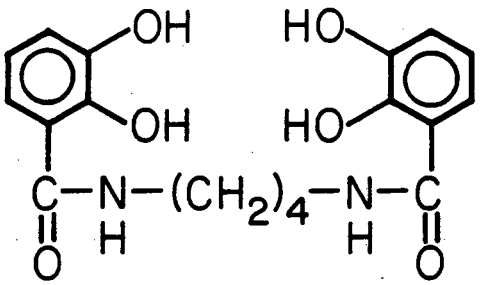

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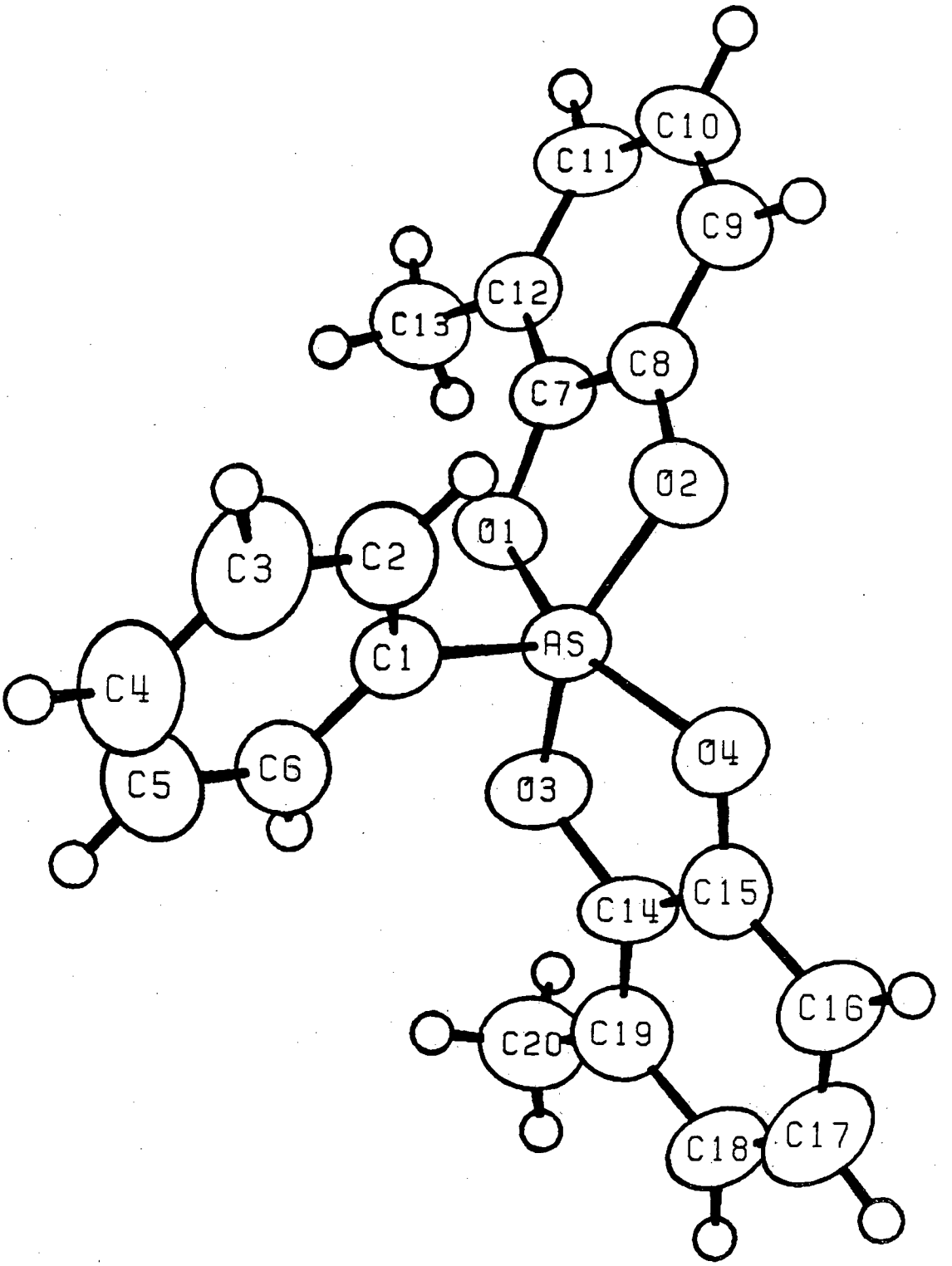
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