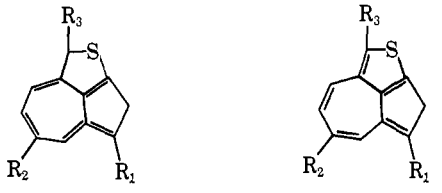
**Table I.** Delocalization Energies Calculated with the HMO and ω-Variation, Self-Consistent-Field Technique[a]

| Molecule | HMO DE | ω-Technique DE |
|---|---|---|
| **1b** | 3.826β | 3.729β |
| **2b** | 3.859β | 3.840β |
| **3a**[b] | 3.664β | 3.574β |
| **4a**[b] | 3.351β | 3.339β |

[a] Reference 3. [b] The S atom was treated according to the technique of H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

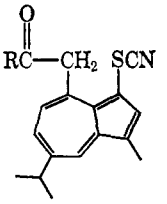
Heterocycles which are analogs of nonbenzenoid aromatic hydrocarbons have been of interest to us for some time. In view of the lower resonance energy of thiophene (28–31 kcal/mole)[4] relative to that of benzene (36 kcal/mole), a heterocyclic analog of **2**, in which a sulfur atom has replaced the $C_3$–$C_4$ ethylenic linkage, might be anticipated to exist as the azulenodihydrothiophene isomer **3a** in preference to the heptafulvenothiophene isomer **4a**. This expectation is supported by the delocalization energies calculated for **3a** and **4a** (Table I).



**3** **4**

**a**, $R_1 = R_2 = R_3 = H$
**b**, $R_1$ = Me; $R_2$ = *i*-Pr; $R_3 = C_6H_5CO$
**c**, $R_1$ = Me; $R_2$ = *i*-Pr; $R_3 = p$-$BrC_6H_4$

It seemed likely that the thiocyanoketone **5a**, which had previously been used to prepare the azuleno[1,8-*bc*]thiapyran ring system,[5] could be converted to the cyclic sulfide **3b** by treatment with base. Treatment of **5a** with a tertiary amine in a polar organic solvent (*e.g.*, dimethyl sulfoxide) or with potassium hydroxide in methanol–ether solution gave a red, crystalline solid, mp 109.5–111°, in good (70–90%) yield. The elemental analysis (*Anal.* Found: C, 79.52; H, 5.96; S, 9.37) and mass spectral molecular weight (332.12) of this substance are in accord with a molecular formula



**5a**, R = $C_6H_5$
**b**, R = $p$-$BrC_6H_4$

of $C_{22}H_{20}OS$ (one molecule of **5** minus the elements of HCN). However, the carbonyl band in the infrared at 6.11 μ and the $\lambda_{max}^{CHCl_3}$ at 504 mμ in the visible are strong evidence that the compound is not the expected **3b**. **3b** should exhibit a normal carbonyl absorption at ~5.9 μ and have a visible spectrum very similar to that of 3,8-dimethyl-5-isopropyl-1-methylthioazulene[6] ($\lambda_{max}$ 654 mμ). The nmr spectrum shows approximately the pattern expected for **3b**. However, the chemical shifts are at higher fields than normally observed for aromatic azulene derivatives, and the broad peak at τ 6.78, which might be assigned to the proton adjacent to the carbonyl group, contains the correct area for two protons. The spectral data are in complete agreement with structure **4b**, 2-benzoyl-5-isopropyl-7-methyl-8H-azuleno-[1,8-*bc*]thiophene.[7]

Additional support of the proposed structure has been obtained from an X-ray crystallographic investigation[8] of a bromine derivative (**4c**), prepared by treating **5b** with pyridine in a similar reaction. Crystals of **4c** belong to the monoclinic system with cell constants of $a$ = 9.063, $b$ = 10.807, $c$ = 19.368 Å, and $\beta$ = 102.38°; space group $P2_1/n$. Full three-dimensional data have been collected with Mo Kα radiation on a General Electric automatic diffractometer. The $R$ factor is presently 0.09. All hydrogen atoms have been located and the determination is in complete agreement with structure **4c**.

The reaction mechanism leading from **5a** to **4b** most probably proceeds *via* **3b** as a labile intermediate followed by a prototropic rearrangement to **4b**. It is interesting to note that our results show that **4b** is more stable than **3b**; this is in opposition to expectations based on the delocalization energies calculated for **4a** and **3a** (Table I). Most likely, the benzoyl substituent on $C_2$ is responsible for this discrepancy in that it is able to interact with the π electrons in the remainder of the molecule only in structure **4b**, and not in **3b**. Evidence for strong conjugative interaction between the carbonyl group and the π system is provided by the rather long wavelength position, 6.11 μ (1637 $cm^{-1}$), of the carbonyl band in the infrared spectrum of **4b**.

**Acknowledgment.** We wish to thank the National Science Foundation for financial support and the Trustees of the California State Colleges for a Special Leave for Research to L. L. R. We also wish to thank Dr. Harmon Brown of Varian Associates for the mass spectral data and Professor James M. Stewart, University of Maryland, for the use of X-ray diffraction facilities.

(4) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 99; L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 303.

(5) L. L. Replogle, K. Katsumoto, and T. C. Morrill, *Tetrahedron Letters*, 1877 (1965).

(6) L. L. Replogle, R. M. Arluck, and J. R. Maynard, *J. Org. Chem.*, 30, 2715 (1965).

(7) The τ 6.78 absorption was assigned to the $C_8$-methylene group.

(8) H. L. Ammon and P. H. Watts, Jr., unpublished work.

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*Received November 17, 1967*

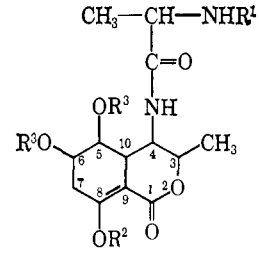
## The Structure of Actinobolin

*Sir:*

In a previous paper[1] the consequence of acid-induced cleavage of the antibiotic actinobolin was described. That information and the evidence derived from the

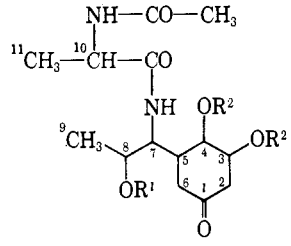
(1) M. E. Munk, C. S. Sodano, R. L. McLean, and T. H. Haskell, *J. Am. Chem. Soc.*, **89**, 4158 (1967).

studies reported in this communication coalesce to generate structure **1** for the intact antibiotic isolated as the stable crystalline sulfate salt, $(C_{13}H_{20}N_2O_6)_2 \cdot H_2SO_4 \cdot 2H_2O$.[2]



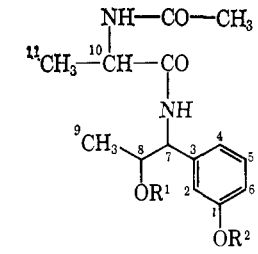
**1**, $R^1 = R^2 = R^3 = H$
**2**, $R^1 = CH_3CO$; $R^2 = R^3 = H$
**3**, $R^1 = CH_3CO$; $R^2 = CH_3$; $R^3 = H$
**4**, $R^1 = R^2 = R^3 = CH_3CO$

Treatment of N-acetylactinobolin[2] (**2**, $C_{15}H_{22}N_2O_7$; mp 254–255° dec; $[\alpha]^{26}D$ +30.0° (*c* 3.8, $H_2O$); $\lambda_{max}^{H_2O}$ 261 mμ (ε 9570), $\lambda_{max}^{0.1NHCl}$ 262 mμ (ε 9370), $\lambda_{max}^{0.1NNaOH}$ 288 mμ (ε 14,300)), the point of departure for the studies described, with 1 *N* aqueous ammonia results in the complete destruction of the chromophore and affords 1 mole of carbon dioxide and N-acetylalanylactinobolone (**5**, $C_{14}H_{24}N_2O_6$;[3,4] mp 161.5–162.5° (resolidifies and melts at 178–180°); $[\alpha]^{25}D$ −57.1° (*c* 3.1, $H_2O$); $\nu_{max}^{KBr}$ 1715 (unstrained ketone C=O), 1665 and 1640 $cm^{-1}$ (amide C=O). The appearance of three one-proton doublets ($J \sim 3.5$–4.0 cps) at δ 4.56, 4.96, and 5.04 in the nmr spectrum[5] (DMSO-$d_6$) that disappear rapidly upon the addition of deuterium oxide indicates three secondary hydroxyl groups. The two amide one-proton doublets at δ 7.50 and 8.04 also disappear upon the addition of deuterium oxide, but at a considerably slower rate.



**5**, $R^1 = R^2 = H$
**6**, $R^1 = CH_3CO$; $R^2R^2 = C(CH_3)_2$

Substantial evidence for the cyclohexanone unit in the actinobolone skeleton derives from the formation of the *meta*-substituted phenyl acetate **7** ($C_{18}H_{24}N_2O_6$; mp 145.5–146.5°; $[\alpha]^{25}D$ −79.0° (*c* 4.1, MeOH); $\lambda_{max}^{EtOH}$ 262 and 269 mμ (ε 300 and 246);[6] $\nu_{max}^{KBr}$ 1770 (aromatic acetate C=O), 1735 (ester C=O), 1670 and 1630 $cm^{-1}$ (amide C=O)) upon treatment with acetic anhydride containing perchloric acid. The *meta* relationship between ring substituents indicated by the pattern of aromatic proton signals in the nmr spectrum (DMSO-$d_6$) is confirmed by the permanganate oxidation of its derivative, **8**, to *m*-methoxybenzoic acid.



**7**, $R^1 = R^2 = CH_3CO$
**8**, $R^1 = H$; $R^2 = CH_3$
**9**, $R^1 = R^2 = H$

The side-chain array at C-5 in N-acetylalanylactinobolone (**5**) is consistent with: (a) the formation of L-alanine upon vigorous acid hydrolysis of **5**; (b) the isolation of L-alanyl-L-threonine from the mild permanganate oxidation of actinobolin; (c) the appearance of a related unit in actinobolamine;[1] and (d) the signal assignments for H-7, H-8, H-9, H-10, and H-11, and their verification by double-resonance experiments, in the nmr spectrum (DMSO-$d_6$) of the O-deacylated aromatic compound **9** as summarized in Table I.

**Table I.** Nmr Assignments and Double-Resonance Experiments[a] for Compound **9**[b]

| Signal irradiated (δ) | Signal obsd (δ) | Multiplicity change |
|---|---|---|
| H-9 (1.00) | H-8 (3.84) | Quintuplet ⟶ d |
| H-11 (1.18) | H-10 (4.40) | q ⟶ s |
| H-8 (3.84) | H-9 (1.00) | d ⟶ s |
| H-8 (3.84) | H-7 (4.58) | d ⟶ s |
| H-10 (4.40) | H-11 (1.18) | d ⟶ s |
| H-7 (4.58) | H-8 (3.84) | Quintuplet ⟶ q |

[a] Field-swept decoupling. [b] After freeze-drying from $D_2O$ several times to exchange H on nitrogen and oxygen for D.

The relationship of the ketone group to the side chain in **5**, suggested by the *meta* arrangement of substituents in **7**, is compatible with the observed facile deuterioxide-induced deuterium exchange of four carbon-bound protons in deuterium oxide solution.[7] In addition, the presence of the $-CH_2COCH_2-$ unit in **5**, as required by this observation, permits the selection of the unsubstituted sites β and γ to the carbonyl for the two uncommitted secondary hydroxyl groups, an assignment supported by the isolation of the isopropylidene derivative **6**, $C_{19}H_{30}N_2O_7$, mp 143–144°.

The loss of only a single carbon atom as carbon dioxide upon mild basic hydrolysis of N-acetylactinobolin (**2**) is in accord with the behavior expected of the β-keto lactone moiety. Further confirmation of the β-keto lactone unit derives from: (a) the formation of enol ether **3**, ($C_{16}H_{24}N_2O_7 \cdot H_2O$; mp 161–163°; $[\alpha]^{26}D$ +29.2° (*c* 2.5, $H_2O$); $\lambda_{max}^{H_2O}$ 264 mμ (ε 10,950); $\nu_{max}^{KBr}$ 1695 $cm^{-1}$ (conjugated lactone C=O)) and (b) the formation of an amorphous pyrazolone **10** ($C_{15}H_{24}N_4O_6$; $\lambda_{max}^{H_2O}$ 243 mμ (ε 6550), $\lambda_{max}^{0.1NHCl}$ 229 mμ (ε 4860), $\lambda_{max}^{0.1NNaOH}$ 236 mμ (ε 5330)),[8] a compound best characterized as its crystalline hexaacetate **11** ($C_{25}H_{34}N_4O_{11}$; mp 129.5–131°; $[\alpha]^{26}D$ −72.3° (*c* 3.2, MeOH)).

(2) T. H. Haskell and Q. R. Bartz, *Antibiot. Ann.*, **1958–1959**, 505 (1959).

(3) Satisfactory elemental analyses have been obtained for all new compounds described herein.

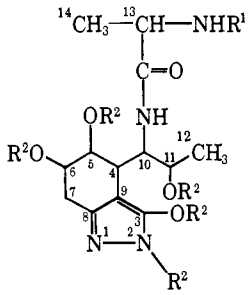
(4) Vigorous basic hydrolysis of actinobolin gives rise to an aromatic compound lacking nitrogen: R. F. Struck, M. C. Thorpe, W. C. Coburn, Jr., and Y. F. Shealy, *Tetrahedron Letters*, 1589 (1967).

(5) Recorded at 60 Mc in the solvent noted in parentheses. Values are reported in δ (parts per million) *vs.* TMS as a reference.

(6) For *m*-cresyl acetate $\lambda_{max}^{EtOH}$ 262 and 269 mμ (ε 324 and 296).

(7) Determined by nmr. Addition of $^-OD$ effects a decrease in area in the δ 1.95–2.45 five-proton multiplet equal to four protons. Only a one-proton signal, assigned to H-5, remains in that region.

(8) N. A. Evans, D. J. Whelan, and R. B. Johns, *Tetrahedron*, **21**, 3351 (1965).



**10**, $R^1 = CH_3CO$; $R^2 = H$
**11**, $R^1 = R^2 = CH_3CO$

The immediate disappearance of two one-proton doublets ($J$ = 4 cps) at $\delta$ 4.77 and 5.05 (in addition to the singlet for the enolic H at $\delta$ 13.15) in the nmr spectrum (DMSO-$d_6$) of **2** upon addition of deuterium oxide confirms the presence of two secondary hydroxyl groups. The formation of the tri-O-acetate **4** ($C_{21}H_{28}N_2O_{10}$; mp 175.0–175.5°; $[\alpha]^{25}D$ +29.4° ($c$ 3.8, MeOH)) lends additional support, while the consumption of 1 mole of periodate by the hydroxylactone (structure **2** with the olefinic linkage saturated, $C_{15}H_{24}N_2O_7$; mp 247–248° dec; $\nu_{max}^{KBr}$ 1730 cm$^{-1}$ (lactone C=O)) derived from **2** by sodium borohydride reduction confirms the vicinal relationship of the two hydroxyl groups in actinobolin as suggested by the product of base hydrolysis.

Evidence linking the lactone carbonyl at C-9 (structure **1**) rather than at the alternate $\alpha$ position, C-7, is obtained by irradiation of the H-6 signal (part of a three-proton multiplet centered at $\delta$ 5.25) in the nmr spectrum ($CDCl_3$) of pyrazolone **11**. This results in the collapse of the methylene proton (H-7) doublet at $\delta$ 3.42 to a singlet as expected.

Finally, a computer analysis[1] of the structural implications of the evidence presented reveals *no* other structure equally consistent with these data; therefore expression **1** for actinobolin is secured.

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## Triphenylphosphine Complexes of Ruthenium and Rhodium. Reversible Combinations of Molecular Nitrogen and Hydrogen with the Ruthenium Complex

*Sir:*

Preparations of tris(triphenylphosphine)cobalt complexes coordinated with molecular nitrogen and some exchange reactions of the nitrogen-coordinated complexes have been reported.[1-3] In nitrogentris(triphenylphosphine)cobalt, the $N_2$ ligand can be readily displaced at room temperature by gases such as hydrogen, ethylene, and ammonia but not by an inert gas like argon.[1] In the course of our study to prepare similar transition metal complexes with an ability to combine with $N_2$, we discovered that a triphenylphosphine–ruthenium complex combines with $N_2$ in a benzene solution and the coordinated $N_2$ ligand can be easily expelled from the ruthenium complex by passing an argon stream through the benzene solution at room temperature. Divalent ruthenium complexes coordinated with $N_2$ are known,[4-6] but no instance of a reversible combination of $N_2$ with a ruthenium complex has been reported.

The ruthenium complex was prepared from $RuCl_3$ or ruthenium(III) acetylacetonate by reduction with triethylaluminum in the presence of triphenylphosphine in tetrahydrofuran or benzene in an atmosphere of nitrogen at room temperature. The light yellow diamagnetic complex obtained was slightly soluble in benzene, toluene, and tetrahydrofuran and was recrystallized from these solvents. The complex slowly decomposes in air.

*Anal.* Calcd for $C_{72}H_{60}P_4Ru$: C, 75.2; H, 5.26. Calcd for $C_{72}H_{62}P_4Ru$: C, 75.1; H, 5.43. Found: C, 75.7; H, 5.53.

The low solubility of the complex in organic solvents hindered the measurement of the nmr spectrum and the molecular weight. The infrared spectrum of the solid complex (Nujol mull) shows the presence of $\nu_{Ru-H}$ at 2080 cm$^{-1}$, which is not detectable in benzene solution. The thermal decomposition, acidolysis, and a reaction with iodine released hydrogen from the Ru complex. From these results a hydride structure must be considered. A monohydride structure $HRu(PPh_3)_4$ is not compatible with the diamagnetism of the complex, and its dimeric structure $[HRu(PPh_3)_4]_2$ appears to be improbable from a steric consideration. Therefore we tentatively propose a dihydride structure $H_2Ru(PPh_3)_4$ for the complex. However, the possibility of a $\sigma$-phenyl monohydride structure,[7-9] $HRu(PPh_3)_3(PPh_2C_6H_4)$, which may be formed by a hydrogen transfer from the *ortho* position of a phenyl group to Ru cannot be excluded.

When nitrogen is bubbled through the benzene solution of the complex at room temperature, the red color of the solution turns brownish and a sharp infrared band appears at 2143 cm$^{-1}$. This band disappears on passing argon through the solution at room temperature accompanied by a color change of the solution from brown to red. The cycle can be repeated many times. A part of the band at 2143 cm$^{-1}$ was shifted to 2110 cm$^{-1}$ when the reaction was carried out with nitrogen containing $^{29}N_2$. From these results we assign the band at 2143 cm$^{-1}$ to the coordinated N–N stretch.[1-6] A similar reversible combination of molecular nitrogen with the ruthenium complex is observed when hydrogen or ammonia is used in place of argon. The $N_2$ ligand is so loosely bound to the complex that,

(1) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 3071 (1967).
(2) A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967); A. Misono, Y. Uchida, T. Saito, and K. M. Song, *Chem. Commun.*, 419 (1967).
(3) A. Sacco and M. Rossi, *ibid.*, 316 (1967).
(4) A. D. Allen and C. V. Senoff, *ibid.*, 621 (1965).
(5) A. E. Shilov, A. K. Shilova, and Yu. G. Borodko, *Kinetika i Kataliz*, 7, 768 (1966).
(6) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).
(7) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967).
(8) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).
(9) G. Hata and A. Miyake, Proceedings of the 10th International Conference on Coordination Chemistry, Tokyo, Nikko, Japan, Sept 12–16, 1967.