usual way afforded a solid which was recrystallized from benzene–hexane to give **1** as colorless crystals. The synthetic material had spectral and chromatographic properties identical with the crystalline bacterial product.

The antibiotic showed pronounced *in vitro* activity against Gram-positive bacteria and *Mycobacterium tuberculosis* H37R but was inactive against Gram-negative organisms. In mice, a single intravenous dose of 25 mg/kg was tolerated but one of 50 mg/kg was instantly lethal; a single subcutaneous dose of 250 mg/kg was tolerated but one of 200 mg/kg failed to protect mice against an experimental acute infection with *Staphylococcus aureus* UC-76.

Acknowledgment. We thank Dr. J. M. Vandenbelt and his staff of these laboratories for the physical measurements, Dr. Carl L. Heifetz of our Detroit laboratories for the biological data, and Dr. H. M. Crooks, Jr., for helpful discussions.

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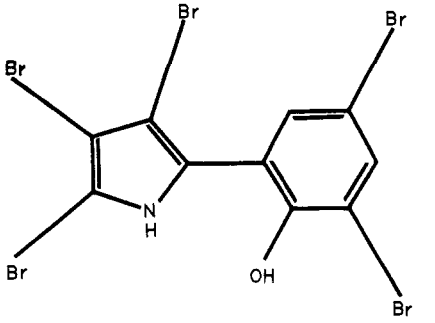

Figure 1. The structure of the antibiotic.

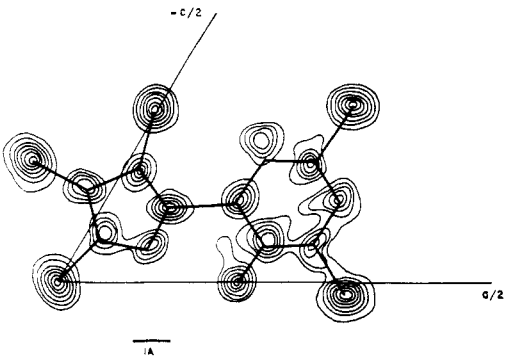

Figure 2. The final electron-density synthesis projected along the *b* axis. Contours are drawn at arbitrary intervals; not all contours are shown in the bromine atoms.

The Structure of a Bromine-Rich Marine Antibiotic

Sir:

The structure of a new antibiotic, $C_{10}H_4NOBr_5$, containing more than 70% by weight of bromine, isolated in the course of studies on marine bacteria,[1] has been determined. Preliminary ultraviolet analysis of the antibiotic had earlier suggested that the molecule might contain a pyrrole ring. This was the only chemical information available during the interpretation of the X-ray results which first established the correct molecular weight.

Table I. Data for the Two Crystal Forms of the Antibiotic

Crystal form	*a*, A	*b*, A	*c*, A	β	D_mD_c g/ml	Space group	*Z*	Mol wt	*V*, A³
Monoclinic laths, elongated along b	22.15	7.47	16.96	108°	2.74	2.76	$P2_1/c$	8	550	2665
Monoclinic tables,[a] elongated along b, lying on (001)	23.04 ± 0.02	3.96 ± 0.05	16.71 ± 0.02	119°20 ± 5	2.76	2.76	Cc	4	552	1328

[a] Crystals used in the X-ray analysis.

Crystals of the antibiotic originally supplied for the X-ray study were very small, thin, monoclinic laths crystallized from chloroform which were unsuitable for the structure analysis. Recrystallization of the material by slow cooling from warm chloroform yielded large monoclinic crystals of a new form which were used for the remaining X-ray work. The unit cell dimensions and space groups of both crystal forms were determined and these results are shown in Table I. The noncentrosymmetric space group Cc was chosen rather than the formally possible C2/c, and this was confirmed when the structure had been determined.

The molecular weights found for the two crystal forms are in good agreement, so it may be concluded that they probably differ only in the packing arrangement of the molecules. The value of 552 ± 5 was confirmed by mass-spectrographic measurements which gave a molecular weight of 553 ± 1.[2] Preliminary chemical analysis had indicated a much higher molecular weight, but a new series of analyses led to the empirical formula $C_{10}H_4NOBr_5$ with mol wt 553.7.

The *b* axis of the unit cell is extremely short, so it appeared probable that the structure would be resolved, without any overlap of atoms, in the projection of the cell along this axis. Consequently, since the purpose of the investigation was to establish the structure of the molecule and accurate bond lengths and angles were not required, the data collection was limited to the *h0l* reflections which were recorded photographically using the Weissenberg multiple film technique with copper radiation. The intensities of 192 reflections

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(2) Dr. D. C. DeJongh, Chemistry Department, Wayne State University, kindly made available the molecular weight decuced from mass-spectrographic studies of the antibiotic.

(90% of the data available) were observable and were estimated visually. The crystal used was small with approximate dimensions 0.40 × 0.13 × 0.05 mm; absorption corrections were therefore neglected.

Positions for the five bromine atoms were obtained from the Patterson projection and were confirmed by means of difference Fourier syntheses. After refinement using a full-matrix least-squares program[3] with isotropic temperature parameters, an electron density synthesis was computed which showed the whole structure to consist of a tribromo-substituted five-membered ring linked by one bond to a dibromo-substituted six-membered having a third substituent light atom.

Both rings were assumed to be unsaturated; this was supported both by the empirical formula and by the projected distances between the bromine atoms. The interpretation of the ultraviolet spectrum was assumed to be correct and the nitrogen was placed as the unsubstituted atom in the five-membered ring. The oxygen atom could not be identified on the basis of peak heights in the synthesis. However, only one position was consistent with an unsaturated six-membered ring and the oxygen was assigned, therefore, as the light atom substituent to the ring, establishing the structure of the molecule as 2-(3,5-dibromophenyl)-3,4,5-tribromopyrrole (Figure 1).

The complete structure was refined by least-squares and the final discrepancy factor was 0.13. The final electron density synthesis is shown in Figure 2 with the structure superimposed.

The proposed structure, which is consistent with all the physical properties of the antibiotic, has been synthesized and shown to be identical in all respects with the antibiotic material.[4]

Acknowledgment. This work was supported through Research Grant GB 2898 from the National Science Foundation.

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Deuterium Isotope Effects in the Photochemistry of 2-Hexanone

Sir:

Substitution of hydrogen with deuterium in organic compounds may exert a marked effect on certain properties of their excited states. Hutchison and Mangrum[1] have demonstrated that substitution of hydrogen in naphthalene by deuterium increases the lifetime of its triplet state 8–9-fold. The deuterium isotope effect on the physical behavior of excited states may, at least in part, be attributed to the differences in the magnitude of the vibrational overlap integral between the ground and the excited states.[5,6] In addition, the usual isotope effect involved in the breaking of a C–D bond may cause a modification in the photochemical behavior of an organic compound. The extent of these isotope effects may depend on how extensively the C–D bond interacts with the excited states. Under the influence of ultraviolet light, ketones with γ hydrogens undergo the type II process and cyclobutanol formation, *i.e.*, the excited carbonyl function interacts with the γ hydrogens exclusively.[7] Recent contributions from various laboratories have demonstrated that these reactions proceed *via* both the $n \rightarrow \pi^*$ singlet and triplet states.[8-11] It was felt that substitution of the γ hydrogen with deuterium may exert an effect on these reactions. This communication deals with the photochemistry of 2-hexanone, 2-hexanone-5-*d*, 2-hexanone-5,5-d_2, and 2-hexanone-d_{12}.[12,13]

The labeled 2-hexanones were synthesized *via* the acetoacetic ester synthesis with the appropriate starting material. The photochemical apparatus used was similar to the one reported by Wagner and Hammond.[8] The filter system consisted of a potassium chromate solution (0.6 g/l. with 0.17 g/l. of KOH added) and Corning 7-54 filters to isolate the 3130-A emission of mercury. The emission intensity was monitored with a ferrioxalate actinometer and found to be 2.4×10^{17} quanta min^{-1} cm^{-2}. Multiple runs were carried out with 2-hexanones in pentane at variable quencher concentrations. The irradiations were interrupted when approximately 10% of the 2-hexanones were decomposed in the absence of the quencher. At this point, negligible amounts of by-products were detected. The progress of reaction and the quantum yields of formation of individual products were followed by quantitative gas chromatography. The reproducibility was found to be better than ±0.003 on the quantum yield determinations. The quencher used was *cis*-1,2-dichloroethylene. When piperylene was used as the quencher, chemical reactions between the deuterated 2-hexanones and piperylene were observed although this was not true in the case of 2-hexanone. The quantum yields of the type II process of the 2-hexanones began to level off and remained constant at moderate to high quencher concentrations. The quantum yields remaining at high quencher concentrations were attributed to the reactivities of the $n \rightarrow \pi^*$ singlet states.[8] The differences between the total quantum yields ($[\Phi]_{total}$) and the quantum yields attributed to the $n \rightarrow \pi^*$ singlet states ($[\Phi]_S$) were taken as the quantum yields due to the triplet states ($[\Phi]_T$). The data for the quantum yields of the type II processes and cyclobutanol formations are summarized in Table I. The Stern–Volmer plots for the type II

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(5) R. P. Frosch and G. W. Robinson, *ibid.*, **38**, 1187 (1963).

(6) W. Siebrand, *ibid.*, **44**, 4055 (1966).

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(11) J. L. Michaels and W. A. Noyes, Jr., *ibid.*, **85**, 1027 (1963).

(12) Some aspects of the photochemistry of 2-hexanone-5,5-d_2 has been reported by R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(13) Photochemistry of 2-pentanone-4,5,5-d_3 and the relative reactivities of its γ-H and γ-D atoms have been reported by R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).