

and 450°C, Figure 2d. The structured absorption at 4000 Å and the continuum at 5100 Å were first reported in 1910,<sup>7</sup> and later<sup>8,9</sup> assigned to either S<sub>3</sub> or S<sub>4</sub>. This assignment has been confirmed by a study of the intensity of this system as a function of vapor pressure and temperature, and by comparison with the mass spectroscopic data<sup>10,11</sup> on the vapor composition. We have now recorded spectra with <sup>34</sup>S and determined that the electronic origin of the 4000-Å system lies at 4235 Å. If one allows for a solvent shift and considers the temperature difference, the Franck-Condon curve and the electronic origin agree very well with those of the absorption of frozen liquid sulfur.

In order to determine whether the absorption, and therefore the red color, was really due to S<sub>3</sub> or S<sub>4</sub>, we decided to prepare small sulfur species in a low-temperature matrix. Sulfur vapor is not a suitable source for the synthesis of S<sub>3</sub> or S<sub>4</sub>, because it always also contains other species.<sup>10,11</sup> Instead we used the photolysis of S<sub>3</sub>Cl<sub>2</sub> in an organic glass and in rare-gas matrices. S<sub>3</sub>Cl<sub>2</sub> was prepared from SCl<sub>2</sub> and liquid H<sub>2</sub>S.<sup>12</sup> In this synthesis only chlorosulfanes with an odd number of sulfur atoms are formed, and S<sub>4</sub>Cl<sub>2</sub> is absent. S<sub>3</sub>Cl<sub>2</sub> 99% pure can be obtained by vacuum distillation. A 10<sup>-4</sup> M solution of S<sub>3</sub>Cl<sub>2</sub> in 1:2 isopentane-cyclohexane at 77°K, with the spectrum shown in Figure 2g, was photolyzed with a high-pressure mercury arc. The spectrum of the photolysis products is shown in Figure 2e. Figure 2f shows the photolysis products of S<sub>3</sub>Cl<sub>2</sub> in a krypton matrix at 20°K. The experimental technique used in the preparation and handling of low-temperature samples was similar to that described elsewhere.<sup>13</sup> The spectrum has a vibrational spacing, a Franck-Condon curve, and an origin as expected for the cold gas species responsible for the absorption of sulfur vapor in Figure 2d. This indicates that the gas species absorbing at 4000 Å is the same as that produced by photolysis of S<sub>3</sub>Cl<sub>2</sub> and is S<sub>3</sub>, thiozone. The mechanism of the photolysis of S<sub>3</sub>Cl<sub>2</sub> yielding thiozone seems to be analogous to that of the photolysis of S<sub>2</sub>Cl<sub>2</sub>,<sup>14</sup> which yields S<sub>2</sub>, and very little S<sub>2</sub>Cl. Whether the continuous absorption at 5100 Å, which also occurs in frozen liquid, is due to S<sub>3</sub> or S<sub>4</sub> has not yet been determined.

The similarity among the matrix spectrum, the vapor spectrum at 450°C, and that of quenched red sulfur indicates that hot liquid sulfur contains S<sub>3</sub>. S<sub>3</sub> and S<sub>4</sub> have similar thermal properties and always occur together.<sup>10,11</sup> Thus, hot liquid sulfur contains S<sub>3</sub> and S<sub>4</sub>.

We conclude that the color change upon heating of sulfur is due to formation of S<sub>3</sub> and S<sub>4</sub>. Comparison of the optical density of vapor and liquid at 4000 and 5100 Å indicates that at the boiling point sulfur contains from 1 to 3% S<sub>3</sub> and S<sub>4</sub>.

Detailed data and analysis will be presented later.

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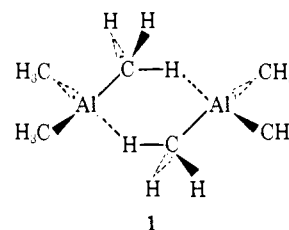
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 Received October 26, 1970

### Crystal Structure and Rotational Barriers of Tricyclopropylaluminum Dimer

Sir:

The structures of dimeric aluminum derivatives are of interest because of the unique bonding present in these systems. The early work of Lewis and Rundle<sup>1</sup> and the more recent work of Vranka,<sup>2</sup> Magnuson,<sup>3</sup> and Malone<sup>4,5</sup> provide data concerning the orientation and bonding of CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, and other bridging groups such as N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. In general, these structures have been considered compatible with the general bonding picture first suggested by Lewis and Rundle<sup>1</sup> and amplified by other calculations, such as those of Levison and Perkins.<sup>6</sup>

After additional calculations on Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> using the data of Vranka and Amma,<sup>2</sup> Byram, *et al.*,<sup>7</sup> have proposed that a hydrogen atom from the bridging methyl group participates strongly in the bridge bond as shown in **1**. The <sup>27</sup>Al nqr studies of Dewar and



Patterson<sup>8</sup> led them, as well as Cotton,<sup>9</sup> to question the proposal of Byram, *et al.*<sup>7</sup> Additional data are required, however, to fully assess the importance of hydrogen participation in the bridge bond.

The puckering of the four-membered ring containing the bridging groups in compounds such as Al<sub>2</sub>(μ-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Me<sub>4</sub> and Al<sub>2</sub>[μ-N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>](μ-CH<sub>3</sub>)(CH<sub>3</sub>)<sub>4</sub> also implies that the terminal methyl groups should be nonequivalent magnetically, giving rise to two nmr signals in the absence of rapid exchange. To date this magnetic nonequivalence of terminal groups in bridged aluminum compounds has not been reported. We now wish to report on the structure determination of tricyclopropylaluminum and on nmr studies of two dimeric species which show terminal group magnetic nonequivalence.

Tricyclopropylaluminum crystallizes in space group P2<sub>1</sub>/c with *a* = 14.573 ± 0.003, *b* = 9.422 ± 0.002,

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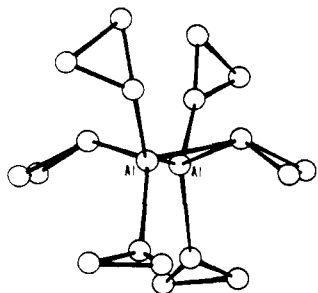


Figure 1. A view of the hexacyclopropyldialuminum molecule.

and  $c = 13.719 \pm 0.006 \text{ \AA}$ ,  $\beta = 81^\circ 54' \pm 2'$ , and with four  $\text{Al}_2(\text{C}_3\text{H}_5)_6$  dimers per unit cell. The calculated density is  $1.07 \text{ g/cm}^3$ . Independent application of the Sayre relation<sup>10</sup> and the conventional Patterson method led to identical solutions. Isotropic least-squares refinement on the 1891 independent reflections collected on a Picker automatic diffractometer in the moving-crystal-moving-counter mode at room temperature led to a conventional discrepancy factor of 0.166. The carbons in one of the terminal cyclopropyl groups refined to high isotropic thermal parameters of 14–17, whereas the other carbons had normal values (6.6–11.2). As a result of the high thermal motion, we were not able to unambiguously identify hydrogen positions from difference synthesis. Inclusion of contributions from calculated hydrogen parameters reduced the discrepancy factor to 0.156. Anisotropic refinement of the carbon and aluminum atomic parameters yielded a discrepancy factor of 0.091.

The large thermal parameters and somewhat disappointing discrepancy factor result from the low melting point ( $60^\circ$ ) of the compound and the fact that the crystal had to be wedged insecurely into a quartz capillary due to the extreme sensitivity of the compound to air, water, and adhesives.<sup>11</sup>

The nmr spectra were obtained on a Varian A-60A nmr spectrometer equipped with low-temperature accessories. The temperature was calibrated against a methanol standard.<sup>12</sup> The solutions were made by introducing  $\text{Al}_2(\text{C}_3\text{H}_5)_6$  into an nmr tube in an argon-filled drybox, then attaching this to a vacuum system and distilling into it known amounts of solvent (toluene) and trimethylaluminum. The tube was then sealed off and kept stored at low temperature.

The structural determination of tricyclopopyl-aluminum shows it to be dimeric as in Figure 1. The Al–Al distance is  $2.618 (3) \text{ \AA}$  as opposed to  $2.600 (4) \text{ \AA}$  in  $\text{Al}_2(\text{CH}_3)_6$ . The average aluminum–bridging carbon distance is  $2.087 (8) \text{ \AA}$ , ranging from  $2.062 (7)$  to  $2.098 (8) \text{ \AA}$ . The average aluminum–terminal carbon bonding distance is  $1.93 (1) \text{ \AA}$  with a range of  $1.90 (1)$ – $1.95 (1) \text{ \AA}$ . The four-membered bridging ring is puckered with a dihedral angle of  $31.9^\circ$  between the two Al–C–Al planes in the ring. This distortion is larger than that found

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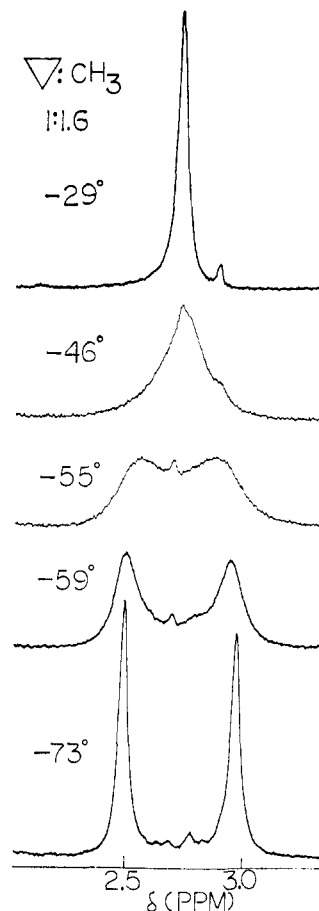


Figure 2. The variable-temperature nmr spectra of the methyl resonances of a tricyclopopyl-trimethylaluminum mixture with a ratio of cyclopropane: $\text{CH}_3$  of 1:1.6 obtained at 60 MHz.  $\delta$  is in parts per million upfield from the methyl resonance of toluene.

in other bridged aluminum systems. The bridging cyclopropyl groups are both bent back on the same side of the ring in such a way that the  $\text{H}_2\text{C}-\text{CH}_2$  bond in each of these rings is approximately parallel to the Al–Al bond.

Using the usual picture for bonding in the cyclopropane molecule with one of the orbitals normally used to bond a hydrogen to the ring pointed at the center of the Al–Al bond, then the plane of the three carbons in a bridging group would make a dihedral angle of  $123.1^\circ$  with the Al–C–Al plane. In fact, these angles are  $135$  and  $134.1^\circ$ , in reasonable agreement with this model. The angle defined by the midpoint of the Al–Al bond, the bridging carbon atom, and the midpoint of the  $\text{H}_2\text{C}-\text{CH}_2$  bond in the bridging cyclopropyl ring is  $135^\circ$ .

The overall idealized symmetry of the  $\text{Al}_2(\text{C}_3\text{H}_5)_6$  molecule is  $C_2$ , with the twofold axis perpendicular to the Al–Al bond. This leaves three rings symmetry independent. This structure and the bonding implied by it is in full accord with that of Rundle,<sup>1</sup> Amma,<sup>2</sup> Stucky,<sup>3</sup> Malone,<sup>4,5</sup> and Dewar<sup>6</sup> and appears to rule out a hydrogen bridge in this molecule.

In order to determine if nonequivalence of terminal groups could be observed in solution, low-temperature nmr studies of  $\text{Al}_2(\text{C}_3\text{H}_5)_6$  were undertaken. Line broadening was observed, but the low solubility and complexity of the cyclopropyl spectrum prevented an unambiguous determination of the effects causing the

line broadening.<sup>13,14</sup> To solve this problem, the spectrum of  $\text{Al}_2(\text{CH}_3)_4(\text{c-C}_3\text{H}_5)_2$ , in which the cyclopropyl groups have been shown to reside in the bridging positions,<sup>15</sup> was investigated as a function of temperature. The spectra for the methyl region obtained between  $-29$  and  $-73^\circ$  are shown in Figure 2.

Preliminary calculations using these data indicate that the activation energy for the process giving rise to equivalent methyl groups is approximately 11 kcal/mol, which is considerably less than the  $\sim 15$  kcal/mol observed for bridge-terminal exchange in  $\text{Al}_2(\text{CH}_3)_6$ .<sup>16</sup> The process is thought to be a rotation inversion of the cyclopropyl group which equates the four terminal methyl groups. This represents the first clear evidence for this process in an electron-deficient aluminum system and suggests that further studies should be carried out on this system, the phenyl-bridged system, and systems such as the phenylethynyl-bridged derivatives,<sup>17</sup> to determine if they also have distorted structures showing nonequivalent terminal groups.

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### Conformation of Tetracycline Ring Systems. Structure of 5,12a-Diacetyloxytetracycline

Sir:

The numerous chemical and structural investigations<sup>1</sup> of tetracycline derivatives include only two single-crystal X-ray structure analyses, namely, the hydrochlorides of Aureomycin<sup>2,3</sup> (**1**, 7-chlorotetracycline) and Terramycin<sup>4,5</sup> (**2**, 5-hydroxytetracycline). These structures, which are very nearly isomorphous, helped to establish the relative configurations of the chiral centers in the molecules and provided a model conformation for the tetracycline ring system. We now report the determination of the structure of the free base, 5,12a-diacetyloxytetracycline<sup>6</sup> (**3**); the molecule has relative chiralities identical with those in 5-hydroxytetra-

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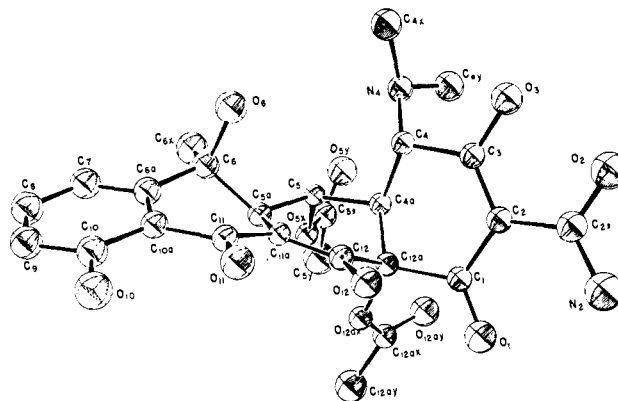
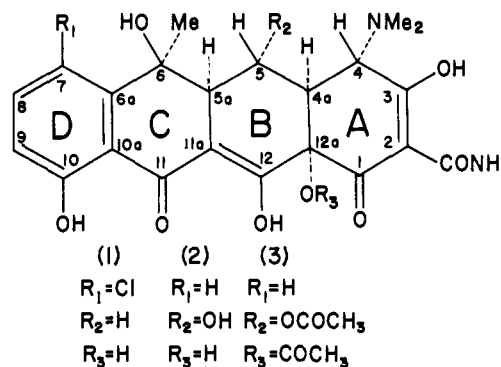


Figure 1. A perspective representation of the structure of 5,12a-diacetyloxytetracycline.

cycline, but it displays a strikingly different molecular conformation.



Excellent crystals which provided data of high quality were obtained by slow evaporation of a 2-propanol solution of material which was prepared and carefully purified by one of us (H. M.). The observed Laue symmetry and extinctions correspond to the orthorhombic space group  $P2_12_12_1$  with  $a = 18.896 \pm 0.010$ ,  $b = 14.229 \pm 0.007$ ,  $c = 9.406 \pm 0.006$  Å;  $Z = 4$ ;  $\rho_{\text{calcd}} = 1.430$  g/cm<sup>3</sup>; and  $\rho_{\text{obsd}} = 1.44$  g/cm<sup>3</sup>. Diffraction intensities were measured in the  $\theta$ - $2\theta$  scan mode with Zr-filtered Mo  $K\alpha$  radiation on a Picker FACS-I diffractometer; of the 3292 independent reflections investigated ( $\sin \theta/\lambda \leq 0.6486$ ), a total of 3124 were retained as objectively observed. No corrections were applied for either absorption or extinction.

The equal-atom structure was solved by direct methods<sup>7,8</sup> using a computerized<sup>9</sup> multiple-solution procedure and tangent-formula<sup>10</sup> phase refinement. Full-matrix least-squares refinement of the structure (157 independent variables) with isotropic thermal parameters yielded a standard residual  $R = 0.101$  for all observed data; a weighted residual  $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$  of 0.104 was obtained with  $w = 1/\sigma^2$ . Nearly all hydrogen positions were determined with good resolution from a difference-Fourier synthesis.

The perspective view shown in Figure 1 displays the essential configurational and conformational features of the molecule. The six chiral centers are (*R*)- $C_4$ , (*R*)- $C_{4a}$ , (*S*)- $C_5$ , (*R*)- $C_{5a}$ , (*S*)- $C_6$ , and (*R*)- $C_{12a}$ . Since the

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