the photoinduced and thermal shifts switch the positions of the two methylene protons?

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**Registry No. 1,** 86088-72-4; **2,** 86088-74-6; **3,** 86088-73-5; **4,** 86101-35-1; Co, 7440-48-4.

**Supplementary Material Available:** Listings of positional and thermal parameters and tables of bond lengths and angles derived from crystallographic analysis of **2** and **3** (6 pages). Ordering information is given on any current masthead page.

## $^{31}P$ Shielding Tensor of Deoxycytidine 5′-Monophosphate

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The use of $^{31}P$ NMR in oriented fibers to test structural models of nucleic acids requires a knowledge of the orientation of the eigenvectors of the $^{31}P$ shielding tensor with respect to the local phosphate skeleton.[1] Previous work along those lines from this laboratory used barium diethyl phosphate[2] (BDEP) and 2-aminoethyl phosphate[3] (AEP) as model compounds: these were the only two for which the orientation of the shielding tensors had been determined. Terao et al. have studied several nucleic acids and nucleotides as powders.[4] Here, we report a single-crystal $^{31}P$ study of deoxycytidine 5′-monophosphate in the free acid form (5′-dCMP) intended to test the generality of the eigenvector orientations used previously and in a structure perhaps more closely related to that found in nucleic acids.

Single crystals of 5′-dCMP were grown by slow evaporation from an aqueous solution. One crystal with dimensions 4 × 4 × 3 mm was mounted on a NMR goniometer head previously described.[5] The experiment was done on a home-built double-resonance spectrometer operating at 68.4 MHz for $^{31}P$ and 168.9 MHz for $^{1}H$. Cross-polarization conditions were established with a 6-μs $^{1}H$ 90° pulse, a 3-ms contact and a 10-15-s delay between successive acquisitions. Typically, 100-150 accumulations were collected for each orientation of the crystal, which was rotated in steps of 9° for a total of 20 data points per axis of rotation. The crystal belongs to the $P_{2_12_12_1}$ space group with four molecules per unit cell,[6] and Figure 1 shows the rotation patterns of the four observed $^{31}P$ resonances.

Table I summarizes the data for the $^{31}P$ shielding tensor of 5′-dCMP along with the corresponding eigenvectors expressed as their direction cosines in a molecule fixed frame. Since the unit cell contains four crystallographically related molecules, a fourfold ambiguity exists in the choice of the orientation of the shielding tensor relative to the molecular frame. Fortunately, only one choice (given in Table I) shows good correlation with the 5′-dCMP molecule as discussed below. Incidentally, the molecule fixed frame shown in Figure 2 corresponds to the one defined by Herzfeld et al. in their study of BDEP[2] and used by Nall et al. in their work on oriented DNA fibers.[1]

As in the case of AEP and BDEP, the principal elements of the shielding tensor in 5′-dCMP show a good correlation with the electron distribution around the $^{31}P$ atom (cf. Figure 2). The most shielded direction ($\sigma_{33}$) lies essentially in the $O_1$-P-$O_2$ plane where a multiple-bond character is expected[7] and is substantiated by the

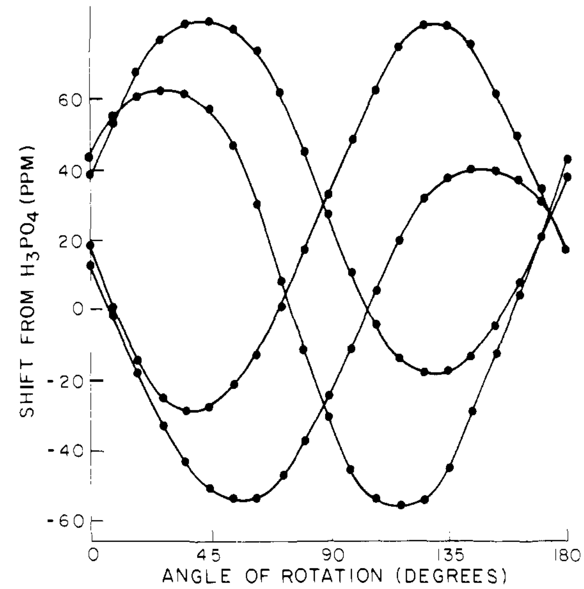


**Figure 1.** Dependence of NMR line positions as a function of rotation of the single crystal about the $y$ axis of the goniometer.

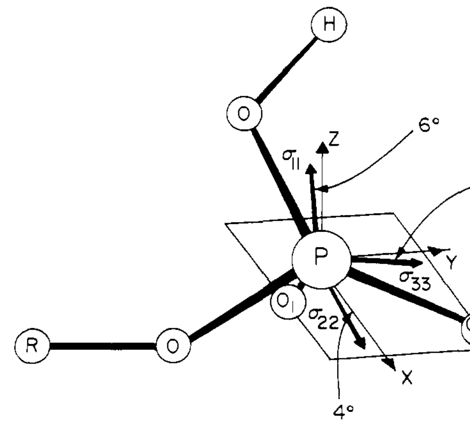


**Figure 2.** Orientation of the $^{31}P$ shielding tensor relative to the molecule fixed frame introduced by Herzfeld and co-workers. The frame is defined as follows: The $z$ axis is perpendicular to the $O_1$-P-$O_2$ plane. The $x$ axis bisects the $O_1$-P-$O_2$ plane. The $y$ axis is chosen as to yield a right-handed system.

Table I. $^{31}P$ Shielding Tensor Principal Values Relative to $H_3PO_4$ and Direction Cosines Relative to the Molecule Fixed Frame[a]

| | | | |
|---|---|---|---|
| $\sigma_{11}$ = 84.5 | −0.053 74 | −0.061 53 | 0.995 0 |
| $\sigma_{22}$ = −5.8 | 0.997 0 | −0.042 12 | 0.049 07 |
| $\sigma_{33}$ = −71.2 | 0.039 55 | 0.994 9 | −0.068 95 |
| $\bar{\sigma}$ = 2.5 | | | |

[a] All values given in ppm with ±2 ppm error. Our results are, within experimental error, in agreement with the values determined by Terao et al. in their powder study of 5′-dCMP.[4]

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(1) B. T. Nall, W. P. Rothwell, J. S. Waugh, and A. Rupprecht, *Biochemistry*, **20**, 1881 (1981).
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relatively shorter bond distances, i.e., $r_{P-O_1} = 1.499$ Å and $r_{P-O_2} = 1.488$ Å. On the other hand, the most deshielded direction ($\sigma_{11}$) lies primarily in the RO–P–OH plane where only a single-bond character is expected[7] and is again substantiated by the relatively larger distances, i.e., $r_{P-OH} = 1.585$ Å and $r_{P-OR} = 1.612$ Å.

As shown in Figure 2, the eigenvectors deviate by less than 10° from the corresponding molecular frame axes. Along with similar findings in BDEP and AEP, these results suggest that $^{31}$P shielding tensors in phosphate esters are rather well aligned with the axes of the molecular frame and thus seem to support the assumption of congruency of the principal axes and molecule fixed frames made by Nall et al. in their study of oriented DNA fibers.

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**Registry No.** 5′-dCMP, 1032-65-1; P, 7723-14-0.

## A Cyclocontraction–Spiroannulation: A Stereoselective Approach to Spirocycles

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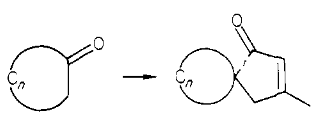
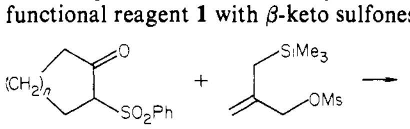
Spirocycles represent challenging targets in both natural product and theoretical chemistry.[1] We report an annulation reaction that is accompanied by a realignment of the initial rings leading to the unusual overall structural change represented in eq 1. In



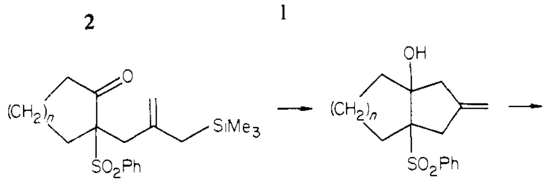
(1)

addition, this sequence illustrates the ability of a sulfone group to function as a leaving group in the presence of Lewis acids, a previously unobserved phenomenon, and the consequent reorientation of a reaction pathway compared to anionic catalysts.

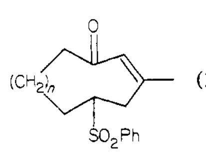
In conjunction with our study of the intercalation of the bifunctional reagent **1** with β-keto sulfones **2** (eq 2),[2] we explored



2 1



3 4



(2)

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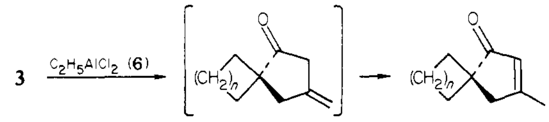
the reaction of **3**[3] with Lewis acids. Performing this reaction with **3** ($n = 8$) and ethylaluminum dichloride (**6**) initially at 0 °C and then allowing it to warm to room temperature led to a 1:1 mixture of the expected product **4** and a second compound that clearly lost the benzenesulfonyl group (eq 3). The same reaction in



(3)

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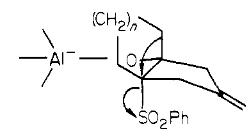
8a, $n = 3$ (97%)
b, $n = 4$ (95%)
c, $n = 8$ (97%)

toluene gave only this latter product. Combustion analysis [found: C, 81.89; H, 11.13] combined with mass spectroscopy ($m/e$ 234) established the formula as $C_{16}H_{26}O$. The symmetry was established by the $^{13}$C NMR spectrum (δ 208.1, 174.6, 128.0, 51.8, 47.5, 32.5 (2), 27.4 (2), 26.0 (2), 25.2 (2), 21.4 (2), 19.3), which combined with the $^1$H NMR (δ 5.74 (sext, $J = 1.3$ Hz, 1 H), 2.3 (quint, $J = 1.3$ Hz, 2 H), 2.05 (q, $J = 1.3$ Hz), 1.2–1.8 (m, 20 H)) and the IR (1687, 1625 cm$^{-1}$) spectrum establishes **8c**[4] as the structure.

A typical preparative procedure involves adding 2 equiv of a 2 M solution of **6** in methylene chloride to 1 equiv of a 0.3 M solution of the β-keto sulfone **3** in the same solvent at room temperature and then refluxing for 3 h. After quenching with ethanol and partitioning between ether and aqueous sodium bicarbonate, the product **8**[4] was isolated pure by simple distillation.

The reaction can be envisioned to involve a pinacol type of rearrangement in which the sulfone group serves as a leaving group in the presence of a Lewis acid as depicted in **9**. That **4** is indeed



9

the intermediate can be demonstrated by treating **3** with the Lewis acid **6** at −78 °C and quenching at that temperature, in which case only **4** is isolated. On the other hand, allowing the solutions to warm prior to quenching leads to the spirocycle **8**. In addition, subjecting **4c** to the normal preparative conditions for the cyclocontraction–spiroannulation also led to **8c**.

Considering the unprecedented ionization of a sulfone induced by an acid catalyst, this reaction proceeds remarkably readily. In the case of **3b** and **3c**, cyclization and ring contraction occur at −40 °C. At these temperatures, the intermediate β,γ isomer **7** is a substantial product as determined by the $^1$H NMR absorptions at δ 5.0 and 4.9 (>=$CH_2$) and 2.9 ($COCH_2C$=) and 2.3 (=$CCH_2C$) for **7c**. The use of refluxing methylene chloride for these cases simply assures complete isomerization of the β,γ isomer **7b,c** to the α,β isomer **8b,c**, which is the slow step in the sequence. The rate of the rearrangement depends on ring size and suggests the optimal alignment depicted in **9** is required. For example, when $n = 3$ the reaction proceeds substantially more slowly—at 0 °C only **4a** is isolated after 0.5 h, at room temperature a 1:1 mixture of **4a** and **8a** is isolated, and only after 2 h at reflux is reaction complete. When $n = 1$, a preliminary examination did not lead to isolation of any of the spiro[3.4]octane system—an observation that may reflect the inability of this short bridge to adopt the anti-periplanar arrangement of the migrating ring bond with respect to the departing sulfone group in this case.

The ability to control stereochemistry in this process depends upon controlling the stereochemistry of the alkylation of the β-keto sulfone. Alkylation of **10** under phase-transfer conditions gives a single diastereomer of the product **11**,[4] whose stereochemistry is assigned by analogy to the alkylation of 2-methylcyclooctanone.[5] Subjecting **11** to the normal conditions gave an 86% isolated yield

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(3) The preferred procedure for the preparation of **3** involves treating 1 equiv of **2** with 1.1 equiv of **1** in the presence of 1 equiv each of KOH, KI, and $[(C_4H_9)_4N]_2SO_4$ in $CH_2Cl_2$–$H_2O$ at room temperature. After dilution with ether and washing with water, drying and evaporation give the crystalline products **3**. See: Samuelsson, B.; Lamm, B. *Acta Chem. Scand.* **1971**, *25*, 1555.

(4) All new compounds have been fully characterized by spectral means and high-resolution mass spectroscopy and/or combustion analysis.

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