stretching mode. This is done by analogy with the spectra of acid salts of carboxylic acids, and other systems with extremely strong O–H···O hydrogen bonds of which the present one is strongly reminiscent, because of the absence of an OH stretching band above 2000 cm^{-1} and the appearance of the strong and broad feature at much lower frequencies.[5] The lack of a distinct mass effect on the latter suggests a disordered proton position in the hydrogen bond.[6] The apparently conflicting situation of having a rather long $R_{O\cdots O}$ but with a spectrum typical of very strong hydrogen bonding may be understood from the ab initio calculation of the potential function of the hydrogen bond in the $H(NO_3)_2^-$ ion.[7] Several other salts of this ion have essentially similar infrared spectra and this is true even of $Ph_4PH(NO_3)_2$ which seems to contain a much shorter hydrogen bond.[8] In order to locate the H-atom of the $H(NO_3)_2^-$ group, and to further elucidate the nature of the H bonding in $CsH(NO_3)_2$, we plan to undertake a single-crystal neutron diffraction study.

Supplementary Material Available: tables of structure factors and of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Work performed at Argonne National Laboratory is under the auspices of the U.S. Energy Research and Development Administration. The financial support of the Boris Kidric Fund is acknowledged by R. G., D. H., and B. O.

(2) G. C. Dobinson, R. Mason, and D. R. Russell, *Chem. Commun.*, 62 (1967).

(3) B. D. Faithful and S. C. Wallwork, *Chem. Commun.*, 1211, (1967).

(4) J. C. Evans, *Spectrochim. Acta*, 17, 129 (1961).

(5) D. Hadzi, B. Orel and A. Novak, *Spectrochim. Acta, Part A*, **29**, 1745 (1973).

(6) D. Hadzi and B. Orel, *J. Mol. Struct.*, **18**, 227 (1973).

(7) R. Gunde, T. Solmajer, A. Azman, and D. Hadzi, *J. Mol. Struct.*, **24**, 405 (1975).

(8) B. D. Faithful and S. C. Wallwork, *Chem. Commun.*, 1211 (1967).

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Neutron-Scattering Spectrum of Cesium Hydrogen Dinitrate[1]

Sir:

As reported in the previous communication,[2] an x-ray diffraction study of cesium hydrogen dinitrate, $CsH(NO_3)_2$, has shown that in this compound the two nitrate ions are almost perpendicular, oriented so that four of the oxygen atoms form a distorted tetrahedron. The location of the proton was not obtained in the x-ray study,[2] but the NO_3^- groups are presumably held together by a hydrogen bond, and this requires that the proton participate in the tetrahedron. This is an unusual bonding situation, and the dynamics of the proton in this compound are thus of unusual interest. Inelastic neutron scattering is a spectroscopic technique which is especially sensitive to proton motions. Accordingly, we have obtained the neutron-scattering spectrum of cesium hydrogen dinitrate and report the results here.

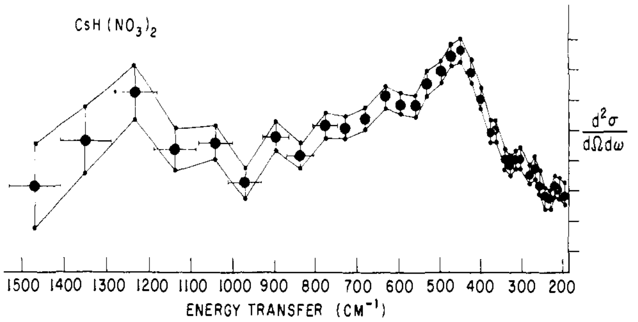

Figure 1. Neutron-scattering spectrum of polycrystalline cesium hydrogen dinitrate. The error bars indicate one standard deviation above and below the observed cross section.

Approximately 30 g of $CsH(NO_3)_2$ was prepared[3] and loaded into an aluminum cell using a glove box. The cell was sealed and mounted in a cryostat cooled with liquid nitrogen. The spectrum was accumulated over a period of 3 days on a time-of-flight spectrometer installed at the ZING prototype pulsed neutron source at Argonne National Laboratory.[4] The results, corrected for scattering by the cell, are given in Figure 1.

The quantity plotted as intensity is the double differential cross section, which is proportional to the sum (over all nuclei) of the squared vibrational amplitudes weighted by the neutron-scattering cross sections.[5] The cross section for light hydrogen is an order of magnitude larger than for other nuclei in the compound, so major peaks in the spectrum are indicative of large-amplitude vibrations of the hydrogen atom. (Smaller peaks reflect vibrations involving other atoms, sometimes enhanced as the hydrogen is carried along.) The major peaks in the cesium hydrogen dinitrate spectrum are at 1240 ± 50 and 450 ± 30 cm^{-1}.

Speakman[6] has designated as type A those acid salts MHX_2 in which the X groups are symmetrically equivalent. Such salts frequently display very short O···O distances and anomalous infrared spectra. The site symmetry[2] of $CsH(NO_3)_2$ is D_2, the pairs of oxygen atoms forming the skewed tetrahedron are related by twofold axes, and the substance is therefore type A.

In some type A substances it has been established[7] that the hydrogen bending modes occur at higher frequencies than the stretching modes. For potassium hydrogen bis(trifluoroacetate) this has been confirmed by a neutron diffraction study[8] which shows the thermal ellipsoid for the hydrogen atom elongated in the direction of the bond. Neutron-scattering peaks attributed to hydrogen motion in these compounds[7b,9] are similar to those observed in $CsH(NO_3)_2$; hence we believe that the peak at ~1240 cm^{-1} represents a pair of bending motions and the ~450 cm^{-1} peak is the stretch. A similar conclusion was reached by Gillard and Ugo[10] in the case of other salts of the hydrogen dinitrate ion.

The position of the proton is not established by either the x-ray diffraction work[2] or the present study; however, the intensity of the satellite peaks at ~1040 and 890 cm^{-1} suggests that the proton is coupled to motions of the NO_3^- groups and therefore is not in the center of the tetrahedron. The calculations of Gunde et al.[11] indicate that the position of lowest potential energy for the proton in this system is on an edge of the tetrahedron, midway between the two groups. The x-ray study[2] shows that two such O···O distances are 2.86 Å and two are 3.05 Å; it is possible that the proton is positioned on the two shorter edges, implying twofold disorder of either a static or dynamic character. If the disorder were dynamic, broadening of the quasi-elastic peak would be observed. In the present experiment, the width of the quasi-elastic peak (fwhm = 0.75 meV) was not perceptibly greater than the instrumental resolution, and we conclude that at 77 K any disorder in this system takes place on a time scale slower than ~10^{-11} s. Further studies to elucidate this question are planned.

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References and Notes

(1) Work performed under the auspices of U.S. Energy Research and Development Administration.

(2) J. M. Williams, N. Dowling, R. Gunde, D. Hadzi, and B. Orel, *J. Am. Chem. Soc.*, preceding paper in this issue.
(3) H. L. Wells and F. J. Metzger, *Am. Chem. J.* **26**, 271 (1901).
(4) J. M. Carpenter, M. H. Mueller, R. A. Beyerlein, T. G. Worlton, J. D. Jorgensen, T. O. Brun, K. Sköld, C. A. Pelizzari, S. W. Peterson, N. Watanabe, M. Kimura, and J. E. Gunning, Proceedings of the Neutron Diffraction Conference, Petten, the Netherlands, Aug 1975. The ZING (zero-gradient-synchrotron intense neutron generator) was a prototype for the proposed IPNS (intense pulsed neutron source), which would have a data-acquisition rate 8000 times as large.
(5) C. V. Berney in "Spectroscopy in Biology and Chemistry", S. H. Chen and S. Yip, Ed., Academic Press, New York, N.Y., 1974.
(6) J. C. Speakman, *Struct. Bonding (Berlin)*, **12**, 141 (1972).
(7) (a) A. Novak, *J. Chim. Phys. Phys.-Chim. Biol.*, **69**, 1615 (1972). (b) D. Hadzi, B. Orel, and A. Novak, *Spectrochim. Acta Part A*, **29**, 1745 (1973).
(8) A. L. MacDonald, J. C. Speakman, and D. Hadzi, *J. Chem. Soc., Perkin Trans. 2*, 825 (1972).
(9) M. F. Collins, B. C. Haywood, and G. C. Stirling, *J. Chem. Phys.*, **52**, 1828 (1970).
(10) R. D. Gillard and R. Ugo, *J. Chem. Soc. A*, 549 (1966).
(11) R. Gunde, T. Solmajer, A. Azman, and D. Hadzi, *J. Mol. Struct.* **24**, 405 (1975).

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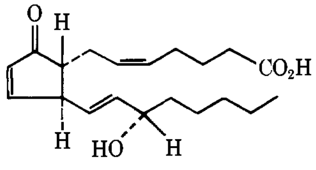
Chiral Synthesis of Prostaglandins from Carbohydrates. Synthesis of (+)-15-(*S*)-Prostaglandin A_2

Sir:

Traditional syntheses of natural prostaglandins[1] involve at least one resolution. We have been devoting some effort to total syntheses of these substances which would not require separation of enantiomers, and now record the first total synthesis of a natural prostaglandin, PGA_2 (**1**)[2] from a simple sugar. The specific route we chose features the use of two Claisen rearrangements: one to produce the necessary trans geometry of a double bond (**3** → **4**) and the other as the means of transferring the chirality of a carbon-oxygen bond to that of a nonadjacent carbon-carbon bond (**5** → **7**).

Reaction of 2,3-isopropylidene-L-erythrose[3] (**2**) with 3 equiv of vinyl magnesium chloride in 1:3 tetrahydrofuran: methylene chloride (4 h, 0°) gave, in 96% yield, the vinyl carbinol **3** bp 97-101° (0.2 mm)[4] which, after protection of the primary alcohol as its methyl carbonate (1.05 equiv of methyl chloroformate in pyridine; 3 h at −30°, 1 h at 0°), bp 106-108° (90% yield), was submitted to Claisen rearrangement by heating with 10 equiv of trimethyl orthoacetate[5] (140°, 3 h with 0.1 equiv of propionic acid; additional 0.05 equiv after 1 and 2 h) to give the unsaturated ester **4** bp 136-138° (0.1 mm) in 83% yield: $[\alpha]^{25}D$ −37.8° (c 1.0, $CHCl_3$); δ 5.43 (H_B, q, J_{AB} = 15 Hz, J_{BC} = 7 Hz), 5.8 (H_A, m).[6]



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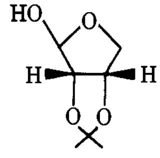

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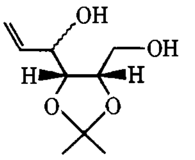

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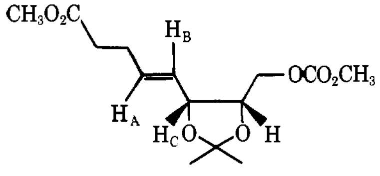

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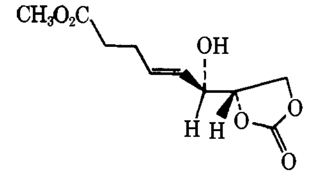
The choice of a chloroformate ester for the protection of the primary alcohol group was essential to the success of the next Claisen rearrangement which requires that the allylic alcohol function, which is masked as its acetonide in **4**, be made selectively available. Indeed, hydrolysis of the acetonide (25% aqueous acetic acid, 120°, 1 h), followed by treatment with triethylamine (1 equiv in methylene chloride, 1 h, 25°) gave the allylic alcohol-cyclic carbonate **5** as a colorless liquid: ν (neat) 3450, ~1790, 1730. Claisen rearrangement of **5** to **7** was now carried out with the orthoester **6**[7] (2 equiv, xylene, 160°, 1 h). After removal of excess side chain (florisil, hexane), the cyclic carbonate function of **7** was hydrolyzed from the resulting trimethyl ester **7** (0.1 equiv of potassium carbonate in dry methanol, 30 min, 25°) and the diol **8** was obtained[8] in an overall yield of 59% from the acetonide **4**.



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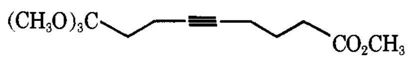

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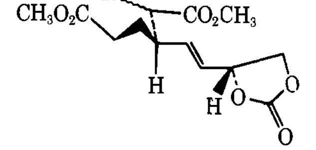

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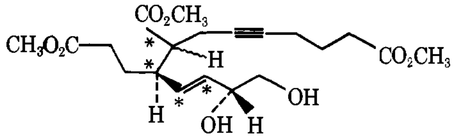

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We were confident that the crucial transfer of chirality implied in **5** → **7** would take place with the carbonate ring equatorial in the chair transition state, as shown in **5***. On the other hand, there is no special steric preference for the