influence product distribution.[12] It is clear, however, that sequential anion formation/mercuration similar to that of Scheme I is required to account for the products as the deuteration experiment established that a dianion of **4** was not formed under the reaction conditions.

The LiTMP/HgCl$_2$ system has potential beyond the cubane case given here. Survey experiments have already demonstrated that the combination rapidly ortho-mercurates N,N-diethylbenzamide and other activated aromatics.[17] The N,N-diisopropylamine of 1-methylcyclopropanecarboxylic acid can also be mercurated in this way.[18] However, the corresponding cyclobutane derivative is inert, an observation appropriate to the significantly lower s character in cyclobutane C–H bonds. Perhaps using stronger bases,[19] we can substitute even such systems.

We are working on the use of other electrophiles and the salts of other metals to trap the ortho anions of suitably activated cubanes. We shall report soon on this, extensions of these reactions, and elaboration of cubylmetallics into new substituted cubanes of substantial interest.

(17) The comination is not unlike that of LiTMP/Me$_3$SiCl in its reactivity toward activated aromatics [Martin, J. C.; Krizan, T. D. *J. Am. Chem. Soc.* **1983**, *105*, 6155]. However, this reagent is not at all effective in substituting cubane amides.
(18) Cf.: Klumpp, G. W.; Kool, M.; Veefkind, A. H.; Schakel, M.; Schmitz, R. F. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 542 and references therein.
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(20) Griffin, G., private communication.

Use of the Pyroelectric Effect To Determine the Absolute Orientation of the Polar Axis in Molecular Crystals

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The presence of a polar axis in a molecular crystal has chemical implications that have only recently begun to be recognized. Thus, the reaction of crystalline p-bromobenzoic anhydride with ammonia gas occurs preferentially in one direction along the polar axis of the crystal.[1,2]

The absolute direction of a polar axis in a polar crystal has thus far been difficult to determine except by the classic method of X-ray anomalous scattering,[1–5] the method employed in the determination of the absolute configuration of chiral crystals. Indeed,

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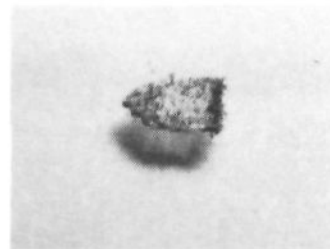

Figure 1. Crystal of p-bromobenzoic anhydride that had been heated, allowed to cool to room temperature, and then sprayed with a jet of a mixture of sulfur, carmine, and lycopodium powder. The polar b axis is right to left with the carbonyl oxygen atoms pointing to the left side of the page. The positively charged lycopodium powder can be seen at the pointed (carbonyl oxygen) end of the crystal and the negatively charged sulfur and carmine at the opposite end, the middle of the crystal being relatively free from the applied powder.

it has been pointed out that the determination of the absolute direction of the polar axis of a chiral crystal provides, in addition, the absolute configuration of the crystal.[1,2,6] We have thus been encouraged to search for other methods, easier to apply, which might provide such information.

A technique making use of the pyroelectric effect[3,4,7] and attributed[3] to Kundt, has long ago been employed as an aid in X-ray structure determination to ascertain whether or not crystalline substances were centrosymmetric. The method consists of blowing through a muslin sieve particles of a mixture of differently colored powders onto a single crystal that has just been heated or cooled. The powders are substances whose particles, as they separate from each other, become electrically charged. (The crystal must be subjected to a change in temperature since the electric dipole of a static polar crystal is likely to have become masked by the accumulation of stray electrostatic charges on its surface.) The positive particles of one substance are attracted to the negative end of the crystal and the negative particles to the positive end. The method seems not to have been employed to determine the absolute direction of the polar axis of a crystal (or even as a device for marking the plus and minus ends once the absolute direction has been determined by some other method).[8] In this paper we describe the application to single crystals of p-bromobenzoic anhydride (whose absolute configuration was previously determined[1,2] by X-ray diffraction employing anomalous scattering) and to some other related compounds and correlate the results with the direction of the reaction with ammonia gas.

Although the powders originally employed were a mixture of sulfur and red lead, we have used a refinement introduced by Hull[9] to analyze the distribution of static electric charge on paper during the manufacturing process. This treatment employs (yellow) flowers of sulfur and (red) carmine as the negatively charged particles and lycopodium powder which had been dyed with methyl violet as those positively charged.[10] This mixture was applied

(6) In Dunitz's words, "Polarity is just one-dimensional chirality" (Dunitz, J. D. "X-ray Analysis and the Structure of Organic Molecules"; Cornell University Press: Ithaca, NY, 1979; pp 129–147).
(7) It has been pointed out[3] that the effect measured in any particular case may not be a pure pyroelectric effect but may contain a contribution from a piezoelectric effect.
(8) We would like to express our indebtedness to researchers at the Central Research Departments of both E. I. du Pont de Nemours and Co. and also at the 3M Co. who a number of years ago provided samples of powders and encouragement to attempt this method. We obtained successful results, however, only much later and with powders prepared as described in this paper.
(9) Hull, H. H. *J. Appl. Phys.* **1949**, *20*, 1157–1159.
(10) A mixture of five parts (by volume) of flowers of sulfur ground and sieved to a particle size of less than 0.063 mm with one part of carmine (Aldrich Chemical Co.) was ground and then mixed with three parts of lycopodium powder (Sargent-Welch Scientific Co.) dyed blue with methyl violet. The crystal to be investigated was heated on a glass slide to 100 °C in an oven and after being allowed to cool was treated with a stream of the powder mixture blown with an atomizer bulb through a muslim sieve. The success of the method depends on sieving the flowers of sulfur to obtain particles of sufficiently small size.
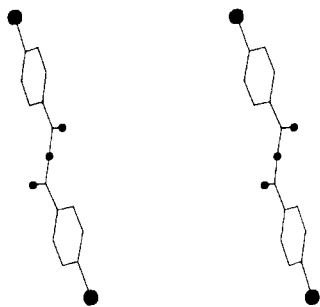
Figure 2. Stereopair drawing of a molecule of *p*-bromobenzoic anhydride. The large black circles are bromine atoms and the small ones are oxygen atoms. The view is down the polar *b* axis. Note that the molecular 2-fold axis is parallel to the crystal's *b* axis (perpendicular to the page) and passes through the central oxygen atom.

to single crystals of *p*-bromobenzoic anhydride with one pointed end shown previously[2] by X-ray anomalous scattering to correspond to the direction toward which the oxygen atoms of the C=O bonds were pointing; the blue (positively charged) particles adhered to the pointed (oxygen) end and the yellow and the red (negatively charged) to the other (carbon) end as shown in Figure 1. Thus it is suggested that the end of the crystal toward which the carbonyl oxygen atoms are pointing is negatively charged and the opposite end along the polar axis positively charged. The molecular dipole moment of benzoic anhydride in benzene solution has been found[11] to be 4.15 D. Determination[12–15] of structures of a number of substituted benzoic anhydrides has shown that the dihedral angle between the two planes containing the carbonyl groups and the central oxygen atom is 47 ± 8°. It seems likely, then, that the preferred conformation of the molecules in the crystal is determined primarily by intramolecular forces rather than by packing and, thus, that the molecules in solution have approximately the same conformation as those in the crystal. Molecules of *p*-bromobenzoic anhydride in the crystal[14,2] lie on a 2-fold crystallographic axis passing through the central oxygen atom and normal to the long molecular axis (Figure 2). The substantial molecular dipole moments of molecules in the crystal are thus aligned along the polar axis of the crystal. To a first approximation the dipole moment of the crystal can be considered to be the vector sum of the dipoles of the individual molecules so that the net moment should have the negative end of the crystal in the direction of the carbonyl oxygen atoms as found.

The related anhydrides of *m*- and *p*-iodobenzoic acid have been found[13] to crystallize in the polar space group *Aba*2 with the conformations of the anhydride molecules similar to that in *p*-bromobenzoic anhydride. The absolute direction of the polar axis of *p*-iodobenzoic anhydride has been determined[13] by anomalous scattering. When the pyroelectric test described above was applied it indicated that the negative end of the polar axis of the crystal was that end with carbonyl oxygen atoms directed toward it as had been found with the *p*-bromobenzoic anhydride. Reaction with ammonia gas showed a preferential reaction at faces at the same (negative) end of the crystal as had also been observed in the reaction of ammonia with *p*-bromobenzoic anhydride. Similar results were obtained with polar crystals of *m*-iodobenzoic anhydride.

Application of the pyroelectric test to crystals of *p*-chlorobenzoic anhydride[15] and *m*-bromobenzoic anhydride[12] known to belong to centrosymmetric space groups showed no separation of yellow

and blue particles, a result consistent with the absence of a polar axis.

Hydrogen Exchange between the Methyl and Hydride Ligands of Cp₂W(H)CH₃ Prior to Methane Elimination

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Alkyl hydride complexes have attracted our interest[1] and that of other research groups[2] because of their potential availability from hydrocarbon activation[3] and their presumed intermediacy in catalytic reactions with hydrocarbon products (e.g., olefin hydrogenation[4]). Alkyl hydrides which eliminate alkanes by simple coupling of the adjacent ligands are, however, rare and confined to the later transition metals.[5] Our attention was therefore attracted by the synthesis of Cp₂W(H)CH₃[6] and by reports that (1) generated Cp₂W upon photolysis under matrix isolation conditions[7] and (2) generated, upon thermolysis in solution, a species (possibly also Cp₂W) capable of C–H bond activation.[6] We now report that (1) under sufficiently dilute conditions intramolecular methane elimination from Cp₂W(H)-CH₃ does indeed occur, and (2) in more concentrated solutions, attack upon the methyl C–H bonds of another Cp₂W(H)CH₃, resulting in hydride hydrogen/methyl hydrogen exchange, competes effectively with methane elimination.

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(2) Alkyl hydride complexes reported before 1979 are listed in ref 1c. Other hydride complexes with monodentate alkyl ligands, in addition to those arising from hydrocarbon activation[3] and olefin hydrogenation,[4] have been reported by: (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (b) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (c) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263. (d) McAlister, D.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966. (e) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500. (f) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221 and references therein. (g) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (h) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580. (i) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831. (j) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (k) Sostero, S.; Traverso, O.; Ros, R.; Michelin, R. A. *J. Organomet. Chem.* **1983**, *246*, 325 and references therein. (l) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7. (m) Kellenberger, B. Ph.D. Dissertation, ETH, Zurich, Switzerland, 1982. (n) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

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(11) Oesper, P. F.; Smyth, C. P. *J. Am. Chem. Soc.* **1942**, *64*, 768–771. This moment is opposed in *p*-bromobenzoic anhydride by components of two C–Br dipoles that make an angle of 70° with the polar axis. Corrected for this, the moment is still approximately 3 D along the polar axis.

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