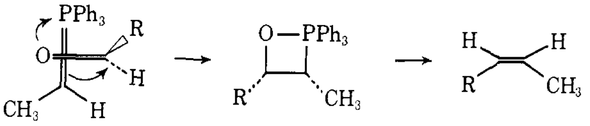
consisted of an unusually broad singlet at δ 62.7 (width at half-height, 15 Hz). Upon warming the sample to −5°, *ca.* 70% decomposition to triphenylphosphine oxide was observed after 5 min and the residual high-field signal was now resolved into two sharp singlets 10 Hz apart, indicating the presence of both cis and trans isomers **6a** and **6b**. The signal of the oxaphosphetane **7** could not be resolved into two components, however, and attempts to resolve the ^{31}P–CH coupling constants of **5**, **6**, and **7** were unsuccessful.

Since the Wittig intermediates from ethylidenetriphenylphosphorane exist >98% in the pentavalent phosphorus form[6] oxaphosphetanes would have to be more stable than betaines if the latter are formed initially under our conditions. However, there is no direct evidence that betaines are involved in nonstabilized ylide reactions.[2a,7] Pending such evidence it is appropriate to focus attention on mechanisms which avoid betaine intermediates, especially since the betaine mechanism fails to account for predominant formation of cis alkenes as listed in Table I and elsewhere.[2b,5,9] We suggest a cycloaddition rationale which requires no ionic intermediates or polar transition states.[10] Orthogonal approach of ylide and aldehyde π bonds in the least hindered orientation would lead directly to the most hindered oxaphosphetane by $_{\pi}2_s + {}_{\pi}2_a$ cycloaddition[11] and would result in selective cis olefin formation. In accord with preliminary experimental results (Table I; also ref 9) this mechanism predicts the highest cis selectivity in Wittig reactions between bulky aldehydes and nonstabilized ylides having unbranched alkyl substituents at the α carbon. The cycloaddition rationale also is consistent with the absence of major solvent polarity effects on the cis:trans ratio[9b] and explains the selectivity of certain oxyylide reactions.[12] Lower cis selectivity in the presence of added lithium salts[2b] may be due to competing formation of the betaine–lithium halide adduct.



Additional studies are under way to test some aspects of the cycloaddition rationale.[14] We are also investigating the influence of solvent, metal salts, and other variables on the structure of Wittig intermediates.

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[6] We have observed analogous pentavalent phosphorus products from methylidenetriphenylphosphorane with cyclohexanone and pivalaldehyde, δ ^{31}P +74.2 and 72.5 ppm, respectively.

[7] The precipitate which forms upon mixing ethereal methylidenetriphenylphosphorane containing lithium bromide with benzaldehyde is believed to be a betaine–lithium bromide adduct.[2,8] We have found that the precipitate is too insoluble in tetrahydrofuran for ^{31}P nmr; the only signal observed is indistinguishable from triphenylphosphine oxide. To our knowledge, the only reported characterization of this precipitate is conversion to styrene at 65° or conversion into a β-hydroxyalkylphosphonium salt by acid, reactions which cannot distinguish between oxaphosphetanes and betaines.

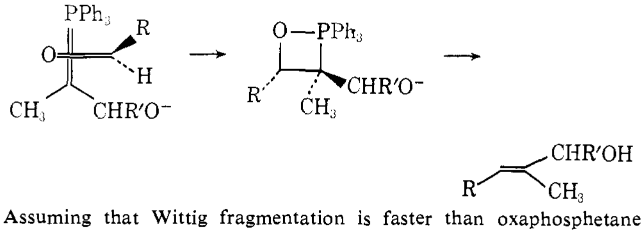
[8] S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).

[9] (a) M. Schlosser, *Top. Stereochem.*, **5**, 22 (1970); (b) L. D. Bergelson, L. I. Barsukov, and M. M. Shemyakin, *Tetrahedron*, **23**, 2709 (1967).

[10] W. P. Schneider, *Chem. Commun.*, 785 (1969).

[11] M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Drieding, *Helv. Chim. Acta*, **53**, 417 (1970); P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).

[12] For oxyylides having a fully substituted ylide α carbon, the favored transition state is chosen to minimize oxygen–oxygen interactions as follows



Assuming that Wittig fragmentation is faster than oxaphosphetane ring opening to the betaine for R = alkyl or aryl (but not for R = H), it is obvious why only one of the two oxygens is lost as triphenylphosphine oxide.[13]

[13] E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226, 3523 6636, 6637 (1970); M. Schlosser and D. Coffinet, *Synthesis*, 380 (1971); 575 (1972).

[14] Kinetic evidence consistent with a cycloaddition mechanism has been reported recently: P. Froyen, *Acta Chim. Scand.*, **26**, 2163 (1972).

[15] Alfred P. Sloan Fellow, 1971–1973.

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An Asymmetric Single-Minimum Hydrogen Bond in the Bifluoride Ion. A Neutron Diffraction Study of *p*-Toluidinium Bifluoride[1]

Sir:

In virtually every experimental study[2–6] of the bifluoride ion, (F–H–F)$^-$, carried out within the past 30 years, the same conclusion has been reached, *viz.*, the anion contains the shortest strongest hydrogen bond known and possesses a symmetrical (centered) hydrogen bond. The symmetrical nature of the hydrogen bond has become accepted as intrinsic to this system, possibly because no one has demonstrated the existence of an asymmetric hydrogen bond in $(HF_2)^-$. However, in the case of KHF_2, Blinc[7] has pointed out some difficulties that arise with the single-minimum symmetric H-bond interpretation. Past studies have been confined mainly to the alkali metal and ammonium bifluorides, in which the anion is located in a symmetrical environment in the crystal. The title compound has been chosen because of the asymmetric crystal environment about the bifluoride ion, which could leave the $(HF_2)^-$ ion free to assume a configuration not obscured by symmetry.

We wish to report the first experimental proof of the existence of a linear asymmetric (single-minimum) hydrogen bond in the (F–H–F)$^-$ ion as derived from a neutron diffraction study of *p*-toluidinium bifluoride.

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Thermodynamic measurements: E. F. Westrum, Jr., and K. S. Pitzer, *J. Amer. Chem. Soc.*, **71**, 1940 (1949); E. F. Westrum, Jr., and G. A. Burney, *J. Phys. Chem.*, **65**, 344 (1961).

[3] Neutron diffraction: S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **20**, 704 (1952); B. L. McGaw and J. A. Ibers, *ibid.*, **39**, 2677 (1963); J. A. Ibers, *ibid.*, **40**, 402 (1964).

[4] Neutron, infrared, and Raman spectroscopy: J. J. Rush, L. W. Schroeder, and A. J. Melveger, *J. Chem. Phys.*, **56**, 2793 (1972); P. A. Giguère and K. Sathianandan, *Can. J. Phys.*, **45**, 2439 (1967), and references therein.

[5] Nuclear magnetic resonance: J. S. Waugh, F. B. Humphrey, and D. M. Yost, *J. Phys. Chem.*, **57**, 486 (1953).

[6] Dielectric measurements: D. Polder, *Nature (London)*, **160**, 870 (1947).

[7] R. Blinc, *Nature (London)*, **182**, 1016 (1958).

The derived distances[8] in $(HF_2)^-$, uncorrected for thermal motion, are F(1)–F(2), 2.260 (4); F(2)–H, 1.025 (6); and F(2)–H, 1.235 (6) Å. This compound crystallizes in the orthorhombic space group $Pbca$, with $Z = 8$ and cell dimensions $a = 7.171$ (4), $b = 18.423$ (11), and $c = 11.839$ (7) Å at 22 ± 2°. The observed and calculated densities are 1.27 and 1.25 g/cm^3, respectively.

Two complete octants (twice the amount required) of three-dimensional data were collected, yielding 2715 reflections [2007 with $(F_o) > 1\sigma(F_o)$], at 22 ± 2° to sin $\theta/\lambda = 0.62$ at the Argonne National Laboratory CP-5 neutron source ($\lambda = 1.142$ (1) Å). All data were corrected for absorption ($\mu = 2.36$ cm^{-1}) and scaled against a standard NaCl crystal. The initial positional parameters for C, N, and F were those given in an X-ray study.[9] All hydrogen atoms were precisely located using Fourier maps. Full-matrix least-squares calculations (with anisotropic thermal parameters and an isotropic extinction correction) have led, at this stage, to a value of the reliability index of $R(F_o) = 0.078$ using all data with $(F_o) > 1\sigma(F_o)$. The present ratio of observations to parameters is 2008:191. A difference Fourier map, calculated to remove all atoms except the hydrogen atom of $(HF_2)^-$, yielded positional coordinates in complete agreement with the least-squares results. A total difference Fourier synthesis was virtually featureless, thus confirming the least-squares results.

The structure is comprised of discrete $CH_3C_6H_4NH_3^+$ cations and $(F\text{–}H\text{--}F)^-$ anions. This is the first known example in which the $(HF_2)^-$ ion, illustrated in Figure 1, possesses an asymmetric hydrogen bond. The F–H distances ($\sigma = 0.006$ Å) and (F–H--F) bond angle of 178.1 (5)° indicate that the anion is essentially linear. The short F–H distance of 1.025 (6) Å is ~0.108 Å longer than in gaseous HF. Finally, the F–F separation of 2.260 (4) Å is identical (±0.01 Å) with that reported for the bifluoride salts of Na$^+$ (2.264 (3) Å),[3] K$^+$ (2.277 (6) Å),[3] and NH_4^+ (2.269 (5), 2.275 (5) Å).[10] The C–C and C–N distances derived in this study agree within the standard deviations reported in the X-ray study ($\sigma = 0.009$ Å).[9]

We feel that the unusual hydrogen bond configuration observed for the anion is a consequence of its very asymmetric near-neighbor (hydrogen bonding) environment. As shown in Table I, atoms F(1) and F(2) each have two near-neighbor H atoms (from $-NH_3^+$ groups of the cation) but with very different F···H(N) distances. Clearly, F(1) is much more rigidly bound than F(2) by strong hydrogen bond formation as is evidenced by its short F···H(N) distances and diminished thermal motion, as illustrated in Figure 1.

Table I. Bifluoride Ion Near-Neighbor Distances

Atom	Neighbors	F···H distances, Å
F(1)	H(N)	1.608, 1.675
F(2)	H(N)	1.777, 2.518

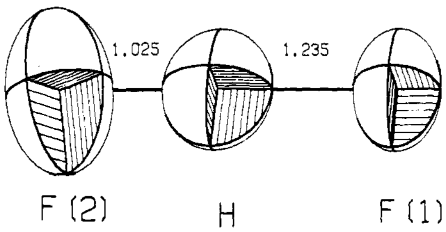

Figure 1. Bond distances in the asymmetric bifluoride ion. The thermal ellipsoids are scaled to enclose 50% probability.

This rather remarkable finding suggests to us that the well-known "symmetric" hydrogen bond only arises whenever the combined electronic and crystal environment about an ion lacks sufficient asymmetry to distort the potential surface "seen" by the bridging hydrogen atom. These results, and those derived from the study[11] of very short (O–H–O) bonds, suggest that regardless of the "shortness" of the X--X bond in the $(X\text{–}H\text{–}X)^{\pm}$ moiety the molecular geometry of the hydrogen bond is strongly dependent on the near-neighbor environment.

Additional investigations including infrared, Raman, and nmr spectroscopic studies are in progress. Deuterated material is being prepared prior to a neutron diffraction study of the isotope effect on the $(F\text{–}D\text{–}F)^-$ bond. The full structural study will be reported at a later date.

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[8] Numbers given in parentheses are estimated standard deviations in the least significant digit of the given parameters.

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[12] CSUI research student with ACEA from the College of Notre Dame, Baltimore, Md.

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Received May 15, 1973

New Heterocyclic Five-Membered Metallo-Ring Complexes of Cobalt and Rhodium

Sir:

Previously, one of the authors showed the formation of five-membered "cobaltacyclopentadiene" complexes by the reaction of substituted acetylenes and cobalt–tolan complex, $\pi\text{-}C_5H_5Co(PPh_3)(PhC{\equiv}CPh)$ (**2a**), which is formally regarded as a three-membered ring compound containing cobalt.[1] Five-membered heterocyclic ring complexes have also been prepared by the reactions of three-membered ring complexes, *i.e.*, dioxygen–, hexafluoroacetone–, and hexafluoroisopropylideneamine–metal complexes with aldehydes, ketones, and hexafluoroisopropylidenamine.[2,3] Recently, an insertion reaction of hexafluoro-but-2-yne and CO molecules into the five-membered cyclic cobalt–azobenzene complex has been reported.[4] These studies suggest that there may be many potential metallo-ring

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[1] H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, 21, 431 (1970).

[2] (a) R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968); (b) P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 92, 5873 (1970); (c) P. J. Hayward and C. J. Nyman, *ibid.*, 93, 617 (1971).

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[4] M. I. Bruce, B. L. Goodall, A. D. Redhouse, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1228 (1972).