pentadienyl rings are pentagonally symmetric and ionically bound in both compounds. Exposure of $Sm(C_5H_5)_2 \cdot C_4H_8O$ to traces of air produces an immediate color change from deep purple to yellow-gray and a drastic reduction in the paramagnetism. Although the resulting material had a relatively sharp X-ray powder pattern, analytical data were not reproducible; consequently, this product was not further characterized.

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A Novel Example of the $[H_5O_2]^+$ Ion. A Neutron Diffraction Study of $HAuCl_4 \cdot 4H_2O$[1]

Sir:

The oxonium ion $(H_3O)^+$ has been postulated for many years to be the dominant protonated species in aqueous acid solution. Its existence in the crystalline state has also been predicted and directly confirmed by X-ray diffraction studies of several acid hydrates. Other aquated proton species such as $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ have also been suggested as possible entities in solution or the crystalline state. The higher species are generally assumed to be aquated oxonium ions, $(H_3O^+ \cdot nH_2O)$. Recently, both neutron and X-ray diffraction studies[2–5] have reported evidence for the first of these, the $H_5O_2^+$ ion, in several crystals. In each case the $H_5O_2^+$ entity has been observed as a nonplanar complex of two H_2O molecules linked by a very short (2.42–2.50 Å) linear hydrogen bond with the bridging proton presumably located at or near the bond center.

We wish to report a novel example of $(H_5O_2)^+$, observed in $HAuCl_4 \cdot 4H_2O$ crystals by neutron diffraction, in which the bridging proton distribution may be described in terms of a double minimum potential. The *bridge* length (O–H–O) in this compound is 2.57 ± 0.01 Å, and the bridge protons are found to be symmetrically disordered about the bond center and, surprisingly, in off-axis locations.

Single crystals of $HAuCl_4 \cdot 4H_2O$ protected in sealed-glass capillaries were examined by X-ray and neutron diffraction techniques. The monoclinic cell parameters are $a = 11.78$, $b = 4.62$, $c = 8.89$ Å; $\beta = 101.9°$; and $Z = 2$. The space group, confirmed by statistical tests and successful refinement, is C2/m. A full three-dimensional neutron structure investigation, utilizing 853 independent reflections measured at λ 1.052 Å on the Argonne computer controlled diffractometer,[6] was carried out. The structure was solved directly from the neutron Patterson function. A chlorine atom disorder in the structure was recognized at the initial Patterson stage. Structure refinement was carried out by Fourier and least-squares methods; the final R factor was 9.7%.

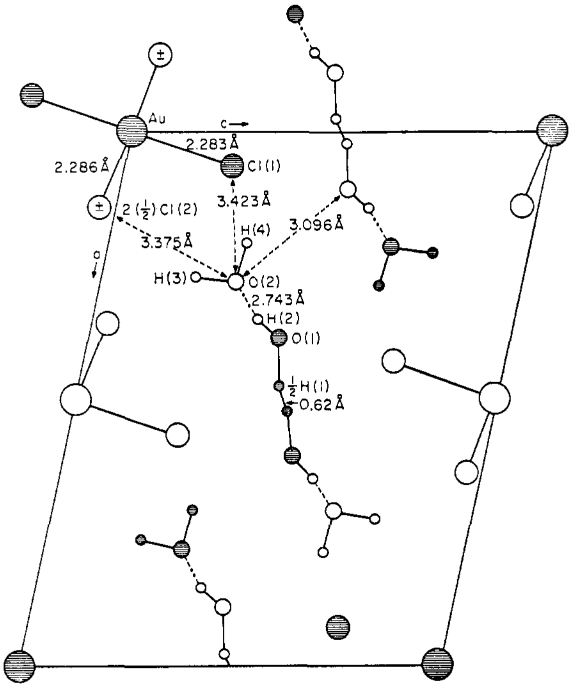

Figure 1. Projection on the *ac* plane of the unit cell contents of $HAuCl_4 \cdot 4H_2O$. Cross-hatched atoms lie in the mirror plane intersecting y at 0. Circles are used to represent atoms which are, in order to decreasing size, Au, Cl, O, and H. The Cl atoms designated ± lie above and below the mirror plane in apparent disorder. The $[H_5O_2]^+$ group consists of two O(1) and two $^1/_2$H(1) atoms in the mirror plane plus two pairs of H(2) atoms which project onto the mirror as two atoms. Dashed lines indicate hydrogen-bonded and other close atom approaches.

The crystal structure, shown in b axis projection in Figure 1, consists of layers, extending parallel to a and b, of square-planar $(AuCl_4)^-$ ions stacked along b with interleaved layers of $(H_5O_2)^+$ ions interconnected by H_2O molecules. The $(AuCl_4)^-$ groups are tilted with respect to the mirror plane which gives rise to the mirror image tilted configuration and the chlorine atom disorder mentioned above. Packing considerations suggest that the $(AuCl_4)^-$ groups are stacked along b in an orderly fashion within one layer; thus the disorder may be attributed to random variations in stacking from layer to layer.

The $(H_5O_2)^+$ groups, distinguished by the short O–H–O bridge distance and the extra proton, are linked by water molecules by means of normal hydrogen bonds (2.74 Å) into infinite chains extended along the b axis. The repeating unit in the chain is $(H_9O_4)^+$ which, as can be seen in Figure 2, has a markedly different configuration than the trihydrated oxonium ion (also $H_9O_4^+$), proposed by Wicke, Eigen, and Ackermann[7] as a major component of aqueous solutions of strong acids. Another unit which may be of significance is the $(H_{14}O_6)^{2+}$ ring shown in Figure 2

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. M. Williams, *Inorg. Nucl. Chem. Letters*, 3, 297 (1967).

(3) J. O. Lundgren and I. Olovsson, *Acta Cryst.*, 23, 966 (1967).

(4) J. O. Lundgren and I. Olovsson, *ibid.*, 23, 971 (1967).

(5) I. Olousson, *J. Chem. Phys.*, 49, 1063 (1968).

(6) M. H. Mueller, L. Heaton, R. A. Aschenbrenner, and L. Amiot, American Crystallographic Association, Minneapolis, Minn., 1967, Abstract E8.

(7) E. Wicke, M. Eigen, and Th. Ackermann, *Z. Physik. Chem.* (Frankfurt), 1, 340 (1954).

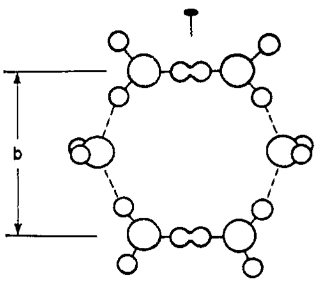

Figure 2. $[H_5O_2]^+$ groups assembled into a ring which is a link of a chain extending along *b*. The repeating unit is $[H_9O_4]^+$. The H_2O molecules which bind the $[H_5O_2]^+$ groups together are rather loosely held and display large thermal motion. Large circles are oxygen and small circles hydrogen atoms.

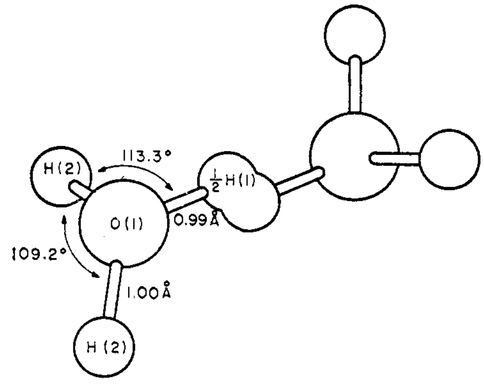

Figure 3. Configuration of the $[H_5O_2]^+$ ion. The two O(1) and the two $^1/_2$H(1) sites are coplanar. The four H(2) sites are symmetry related. The group configuration is strictly *trans*. The O–O separation is 2.57 ± 0.01 Å and the O–H···O angle is 172°.

which is a link in the protonated water molecule chain. Hydrogen-bonding interactions between adjacent chains as well as those between adjacent $(AuCl_4)^-$ and $[(H_5O_2)^+\cdot 2H_2O]$ layers appear to be weak or absent.

The most interesting structural feature is the $(H_5O_2)^+$ group which is illustrated in Figure 3. The required symmetry of the group is 2/m and the configuration is *trans* as indicated. The bridging proton, originally expected to be centered, definitely refined to disordered, off-bond-line positions with a site separation of 0.62 Å.

This rather remarkable configuration raises interpretative problems. There is an intriguing similarity between the now well-known pyramidal oxonium ion and the two symmetry related halves of the $(H_5O_2)^+$ group described here. This suggests that $(H_5O_2)^+$ is simply $(H_3O^+\cdot H_2O)$. The static disorder which this implies and the nonequivalence of the three O–H···O bonds involved tend to weaken this interpretation. We prefer to consider the grouping a variant of the diaquated proton[8] with an unusual symmetrical double-well potential. The dynamic disorder implied in this interpretation should be verifiable by spectroscopic measurements. Such measurements are now in progress.

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[8] J. M. Williams, "Proceedings of the Second Materials Research Symposium, 1967," Special Publication No. 301, National Bureau of Standards, Washington, D. C., in press.

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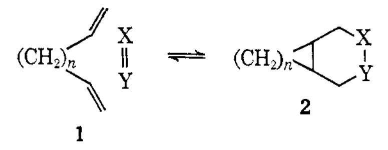
The Geometry of the Transition State of the Retrograde Homo Diels–Alder Reaction. A Stereospecific Conversion of 1,3- to 1,4-Dienes[1]

Sir:

The efficiency with which a small ring transmits conjugative and orbital symmetry influences can be evaluated from a knowledge of the stereochemistry of the homo Diels–Alder reaction (**1** ⇌ **2**). The present work describes a solution of this problem for the retrograde (**2** → **1**) monohomo case (*n* = 1).[2] The results demonstrate that a cyclopropane ring exerts strict control of the stereochemistry of the olefinic product, even in the face of strongly countervailing steric effects. They also provide a stereospecific synthetic method for homologation of 1,3-dienes to 1,4-dienes.



Model studies of ordinary Diels–Alder retrogression show a high degree of stereospecificity. Thus, oxidation of the *cis* hydrazo compound **3** by air, or preferably of an ether solution by yellow mercuric oxide or manganese dioxide in the presence of anhydrous sodium sulfate at 25°, gives a nearly quantitative yield of nitrogen, presumably *via* the very unstable azo compound **4**. Vapor chromatography (vpc) of the solution shows *trans,trans*-2,4-hexadiene (**5**) as the only volatile organic product under analytical conditions that would reveal 0.1% *cis,trans*- or *cis,cis*-2,4-hexadiene. Similarly, oxidation of *trans*-hydrazo compound **6** gives only *cis,trans*-2,4-hexadiene (**8**).[3–8] The ultraviolet chromophore of the presumed azo compounds **4** and **7** is not observed, even at −50°. The exceptionally high rate[9] and stereospecificity suggest double bond participation in both the rate- and product-determining steps of the decomposition of **4** and **7**. Although one cannot strictly exclude a two-step mechanism with an intermediate (*e.g.*, **11**) in which loss of nitrogen is much faster than bond rotation, a simple and conceptually economical alternative would picture the reaction as a concerted, orbital-symmetry-allowed[10] retro-Diels–Alder process.

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[1] This work was supported in part by grants from the Petroleum Research Fund and the AFOSR (SRC)-OAR, U. S. Air Force Grant No. 68-1358.

[2] During our study, W. L. Mock, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P-20, reported some stereochemical results of the analogous decomposition of 3-bicyclo[3.1.0]thiahexane 3,3-dioxides.

[3] Hydrazo compounds **3** and **6** result from hydrolytic decarboxylation of the corresponding esters, **9**[6] and **10**.[5] Compound **9** is formed in virtually quantitative yield from the reaction of **5** and dimethyl azodicarboxylate;[6] **8** and dimethyl azodicarboxylate react more sluggishly to give a 4:1 mixture of **10** and **9** (boiling benzene, 18 hr).

[4] Diazenes[7] and sulfolenes[8] behave analogously.

[5] Elemental analysis confirms the composition.

[6] R. Daniels and K. A. Roseman, *Tetrahedron Letters*, 1335 (1966).

[7] D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1335 (1966).

[8] (a) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966); (b) W. L. Mock, *ibid.*, **88**, 2857 (1966).

[9] Saturated analogs do not decompose at appreciable rates below 140° (see, *inter alia*, P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968)].

[10] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 15 (1968).