Theoretical determination of molecular structure and conformation. II. Hydrogen trioxide—a model compound for studying the conformational modes of geminal double rotors and five membered rings

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The internal rotational surface of hydrogen trioxide has been calculated with the Hartree-Fock method using basis sets with and without polarization functions and optimizing all structural parameters. These calculations have been repeated at the level of Rayleigh-Schrödinger-Müller-Plesset (RS-MP) perturbation theory in order to study the role of correlation effects on barrier values and structures. The relative energies as well as the computed geometrical parameters underline the importance of polarization functions. Although the intrapair correlation contributions significantly stabilize the planar conformations of H₂O₂, the net effect of correlation effects on the conformational potential is moderate because of well-balanced interpair contributions of opposite sign. As in the case of H₂O₂, the correlation effect on the relative energies further decreases if the basis set is improved. On the other hand, reliable structural parameters can only be achieved at the RS-MP level by employing a large augmented basis. The calculated equilibrium RS-MP structural parameters of H₂O₂ are: R(OO) = 143.9 pm, R(OH) = 97.2 pm, α(OOO) = 106.3°, β(OOH) = 100.2°, θ = 78.1°. Bond angles and OO bond lengths are strongly coupled to the rotational angles. A simultaneous rotation of both OH bonds is hindered by large barriers of 22.5 and 11.3 kcal/mole. These potential maxima can be surrounded in a stepwise flip-flop rotation of the OH groups. The barriers of this rotational process turn out to be the saddlepoint energies (6.5 and 5.4 kcal/mole) of the internal rotational surface. It is shown that a close relationship exists between the flip-flop rotation of the geminal double rotor and the pseudorotation of five membered rings. Using the calculated conformational potential V(θ₁,θ₂), the prediction is made that the envelope form of 1,2,3-trioxolane is more stable than the corresponding twist form.

I. INTRODUCTION

The simplest molecular double rotor is hydrogen trioxide, the third member of the homologous series of hydrogen polyoxides beginning with H₂O and H₂O₂. In recent years interest in hydrogen polyoxides has increased due to the positive identification of the long postulated species H₂O₂ and H₂O₃⁴ and the isolation of alkylated derivatives such as (CH₃)₂COOC(C₂H₅)₂ and CF₃OOOCF₃. In addition, H₂O₂ has been found to act as a hydroxylating agent in the superacid medium, thus opening new methods of organic synthesis.⁴ Organic trioxides have been postulated to be intermediates in the ozonolysis of a variety of organic substrates.⁵ Nevertheless, the extreme reactivity of H₂O₂ has prevented any deeper insight into its molecular structure and its conformational behavior.

However, theory does not have to struggle with the limitations of experiment and can provide needed accurate data on H₂O₂ if the various effects of the type of theoretical model employed are carefully taken into consideration.

Apart from a more general chemical interest in H₂O₂, the actual objectives of this study are threefold. First, we want to investigate changes in electronic structure due to the incorporation of an oxygen atom in the OO linkage of hydrogen peroxide. Obviously, an accumulation of oxygen atoms in immediate or close vicinity leads to dramatic effects on structure, conformation, and stability which are normally explained by enhanced lone pair repulsion. This is related to the anomeric or rabbit's ear effect.⁶ Secondly, a systematic evaluation of the conformational profile of H₂O₂ promises to provide a simple way to gain knowledge about the coupling mechanism between the individual rotors. Certainly, the electronic peculiarities of a rotating hydroxyl group influence the conformational tendencies of H₂O₂. This has to be analyzed in order to come to more general conclusions concerning the rotation of double rotors. Finally, H₂O₂ provides a useful model compound for 1,2,3-trioxolanes which have been postulated as intermediates in the ozonolysis of olefines.⁷ Various predictions with regard to the conformation of these five membered rings have been made in order to explain the stereochemical course of the ozonolysis reaction. A complete knowledge of the conformational potential of H₂O₂ should be helpful in understanding the nature of 1,2,3-trioxolanes.

So far, only three limited ab initio studies of H₂O₂ have been reported in the literature,⁸–¹⁰ all of them at the Hartree–Fock (HF) level of theory. They employed small or medium sized basis sets of the minimal,⁸¹⁰ split valence⁸,⁹ or double-zeta³ type to describe the rotational minimum of the molecule. While Radom et al.,⁶ used standard geometries in their calculation of H₂O₂, partial optimization of the geometrical parameters has been undertaken by Azman et al.,¹⁰ (bond angles) and Newton et al.⁷ (bond angles plus OO distance). However, a complete structure determination at the HF level is still missing, not to speak of a systematic exploration of the conformational surface. Furthermore, the question of whether polarization functions play an equally important role in HF calculations on H₂O₂ as they do...
for H₂O₃ has not been investigated previously. Also, no correlation corrected ab initio study of H₂O₃ has been reported.

In order to deal with these questions we have calculated distinct points of the conformational surface with various basis sets ranging from the minimal STO-3G basis to an optimum scaled augmented basis of 67 contracted Gaussian type functions (GTF). In addition, the conformational surface has been explored as a function of two rotational angles using a 60° grid. For each H₂O₃ conformation all geometrical parameters have been optimized. This procedure has been repeated with the Rayleigh–Schrödinger (RS) perturbation theory in order to correct energies and structures for possible correlation errors.

In Sec. III, the results of our ab initio calculations are discussed with regard to the predictions of various simple molecular orbital (MO) models of H₂O₃. In Sec. IV, the computed structural and conformational details of H₂O₃ are compared with those of H₂O₂. Sections V and VI deal with the basis set and correlation effects found for the various conformations of H₂O₃. Next, the form of the internal rotational potential is analyzed in Sec. VII, using various Fourier expansions. In Sec. VIII, possible modes of internal rotation are investigated with the aid of the computed energy contour map. A comparison with the pseudorotation of five membered rings is made. In specific, a parallel is drawn between the conformational tendencies of H₂O₂ and 1,2,3-trioxolane. Finally, in Sec. IX, common features of the conformational behavior of X(OY)₂ molecules are discussed.

II. COMPUTATIONAL DETAILS

As in the first paper of this series²³ we have used standard restricted Hartree–Fock (RHF) theory for closed shell molecules.¹¹ In order to make an assessment of the true HF energy of H₂O₃ the augmented (9s5p1d/4s1p) [4s3p1d/2s1p] basis set of Dunning¹² has been employed. In paper I, optimum scale factors have been reported for this basis using H₂O₂ as a reference molecule. Results of this rescaled version of Dunning’s contracted GTF basis (henceforth called Basis D) are compared with those of three other basis sets, namely A, B, and C: Basis A and B are Pople’s minimal STO-3G¹³ and split valence [3s2p/2s] basis sets.¹⁴ Basis C is also a split valence basis which is augmented by six 3d GTF’s thus giving a [3s2p1d/2s] basis.¹⁵

Correlation effects have been evaluated by the Möller–Plesset (MP) version of the Rayleigh–Schrödinger (RS) perturbation theory.¹⁶ Second order RS–MP energies provide a reasonable estimate of correlation energies. They can be compared with the results of CI calculations including all double substituted configurations.¹⁷

All calculations have been performed with the program COLOGNE 76 which is a modified and improved version of GAUSSIAN 70.¹⁸ COLOGNE 76 allows the efficient optimization of geometrical parameters with a quasi-Newton algorithm.¹⁹ Structural parameters thus obtained are accurate to 0.2 pm and 0.2°.

III. RELATIVE STABILITIES OF DISTINCT CONFORMATIONS OF H₂O₃

Tables I and II summarize RHF energies and structures of seven distinct H₂O₃ conformations which are located at minima, maxima, and saddlepoints of the two-dimensional R(θ₁, θ₂) surface. For all basis sets considered, the planar forms with syn-periplanar (sp) or anti-periplanar (ap) OH groups correspond to conformational maxima while those conformations with at least one OH

<table>
<thead>
<tr>
<th>TABLE I. Absolute and relative RHF energies of minima, maxima, and saddlepoints of the conformational surface of H₂O₃.</th>
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</thead>
<tbody>
<tr>
<td><strong>Point</strong></td>
</tr>
<tr>
<td><strong>Absolute Energies (hartree)</strong></td>
</tr>
<tr>
<td>GMIN</td>
</tr>
<tr>
<td>GMAX</td>
</tr>
<tr>
<td>LMIN</td>
</tr>
<tr>
<td>LMAX1</td>
</tr>
<tr>
<td>LMAX2</td>
</tr>
<tr>
<td>S¹</td>
</tr>
<tr>
<td>S²³</td>
</tr>
<tr>
<td><strong>Relative energies (kcal/mole)</strong></td>
</tr>
<tr>
<td>GMIN</td>
</tr>
<tr>
<td>GMAX</td>
</tr>
<tr>
<td>LMIN</td>
</tr>
<tr>
<td>LMAX1</td>
</tr>
<tr>
<td>LMAX2</td>
</tr>
<tr>
<td>S¹</td>
</tr>
<tr>
<td>S²³</td>
</tr>
</tbody>
</table>

*Geometrical parameters obtained with basis C have been used. The effect of rescaling²² amounts to 0.00277 (GMIN), 0.00287 (GMAX), and 0.00429 hartree (LMAX1).

¹Saddlepoint energies have been approximated for basis A and B, by setting θ₁(S¹) = 0° and θ₂(S²³) = 180°, respectively, and optimizing the remaining geometrical parameters. In the case of the basis C, the rotational angles have been taken from the Fourier analysis described in Sec. VII.
TABLE II. Geometrical parameters of \( \text{H}_2\text{O}_3 \) obtained at the HF level with basis sets A, B, and C (bond lengths in pm, angles in degrees).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GMIN</th>
<th>GMAX</th>
<th>LMIN</th>
<th>LMAX1</th>
<th>LMAX2</th>
<th>S1*</th>
<th>S2*</th>
</tr>
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<tbody>
<tr>
<td>( \theta_1 )</td>
<td>84.2</td>
<td>84.2</td>
<td>84.2</td>
<td>139.2</td>
<td>139.2</td>
<td>139.2</td>
<td>139.2</td>
</tr>
<tr>
<td>( \theta_2 )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>140.5</td>
<td>140.5</td>
<td>140.5</td>
<td>140.5</td>
</tr>
<tr>
<td>( R(\text{O}_1\text{O}_2) )</td>
<td>96.0</td>
<td>96.0</td>
<td>96.0</td>
<td>139.3</td>
<td>139.3</td>
<td>139.3</td>
<td>139.3</td>
</tr>
<tr>
<td>( R(\text{O}_2\text{O}_3) )</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0</td>
<td>140.5</td>
<td>140.5</td>
<td>140.5</td>
<td>140.5</td>
</tr>
<tr>
<td>Basis A, STO-3G</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>( \alpha(\text{OOO}) )</td>
<td>105.9</td>
<td>105.9</td>
<td>105.9</td>
<td>99.0</td>
<td>99.0</td>
<td>99.0</td>
<td>99.0</td>
</tr>
<tr>
<td>( \beta_1(\text{HO}_2\text{O}_3) )</td>
<td>102.5</td>
<td>102.5</td>
<td>102.5</td>
<td>102.5</td>
<td>102.5</td>
<td>102.5</td>
<td>102.5</td>
</tr>
<tr>
<td>( \beta_2(\text{HO}_2\text{O}_3) )</td>
<td>100.1</td>
<td>100.1</td>
<td>100.1</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
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<tr>
<td>Basis B ( {3s2p/2s} )</td>
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<td></td>
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<tr>
<td>( \theta_1 )</td>
<td>88.5</td>
<td>88.5</td>
<td>88.5</td>
<td>142.9</td>
<td>142.9</td>
<td>142.9</td>
<td>142.9</td>
</tr>
<tr>
<td>( \theta_2 )</td>
<td>145.3</td>
<td>145.3</td>
<td>145.3</td>
<td>117.4</td>
<td>117.4</td>
<td>117.4</td>
<td>117.4</td>
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<tr>
<td>( R(\text{O}_1\text{O}_2) )</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0</td>
<td>144.9</td>
<td>144.9</td>
<td>144.9</td>
<td>144.9</td>
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<tr>
<td>( R(\text{O}_2\text{O}_3) )</td>
<td>96.2</td>
<td>96.2</td>
<td>96.2</td>
<td>146.7</td>
<td>146.7</td>
<td>146.7</td>
<td>146.7</td>
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<tr>
<td>Basis C ( {3s2p1d/2s} )</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>( \theta_1 )</td>
<td>93.6</td>
<td>93.6</td>
<td>93.6</td>
<td>138.6</td>
<td>138.6</td>
<td>138.6</td>
<td>138.6</td>
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<tr>
<td>( \theta_2 )</td>
<td>138.9</td>
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<td>138.9</td>
<td>105.9</td>
<td>105.9</td>
<td>105.9</td>
<td>105.9</td>
</tr>
<tr>
<td>( R(\text{O}_1\text{O}_2) )</td>
<td>140.4</td>
<td>140.4</td>
<td>140.4</td>
<td>135.9</td>
<td>135.9</td>
<td>135.9</td>
<td>135.9</td>
</tr>
<tr>
<td>( R(\text{O}_2\text{O}_3) )</td>
<td>95.3</td>
<td>95.3</td>
<td>95.3</td>
<td>140.0</td>
<td>140.0</td>
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<td>140.0</td>
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<tr>
<td>( \alpha(\text{OOO}) )</td>
<td>130.6</td>
<td>130.6</td>
<td>130.6</td>
<td>103.5</td>
<td>103.5</td>
<td>103.5</td>
<td>103.5</td>
</tr>
<tr>
<td>( \beta_1(\text{HO}_2\text{O}_3) )</td>
<td>104.7</td>
<td>104.7</td>
<td>104.7</td>
<td>103.5</td>
<td>103.5</td>
<td>103.5</td>
<td>103.5</td>
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<tr>
<td>( \beta_2(\text{HO}_2\text{O}_3) )</td>
<td>103.6</td>
<td>103.6</td>
<td>103.6</td>
<td>103.5</td>
<td>103.5</td>
<td>103.5</td>
<td>103.5</td>
</tr>
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</table>

*See note b in Table I.

group in an orthogonal (og) position lead to a point of favorably low energy corresponding either to a surface minimum or a saddlepoint. The zero point of energy is taken to be the energy of the (og,og) form which sits at the global minimum (GMIN) of the conformational surface. A second point of low energy can be found for the (+og, -og) conformation representing a local minimum (LMIN) of \( E(\theta_1, \theta_2) \). A global maximum (GMAX) and two local maxima (LMAX1 and LMAX2) of the conformational surface result from the (sp, sp), the (ap, ap), and the (sp, ap) conformation, respectively. Finally, the saddlepoints S1 and S2 are occupied by the (sp, +og) and (+og, ap) forms of the \( \text{H}_2\text{O}_3 \) molecule. Because of the \( C_{2v} \) symmetry of the potential surface, each conformation shown in Fig. 1 possesses one or several symmetry equivalents. Within the section \(-180^\circ \leq \theta_1, \theta_2 \leq +180^\circ\), a total of 25 points with the unique energy properties of the seven conformations of Fig. 1 can be found.

The existence of a (og,og) global minimum for \( \text{H}_2\text{O}_3 \) is rationalized on the same basis as that used to rationalize the structure of \( \text{H}_2\text{O} \) or the equilibrium conformation of \( \text{H}_2\text{O}_2 \). In the oxygen atom, the two singly occupied orbitals \( (2p_x, 2p_y) \) are at right angles to one

FIG. 1. The hydrogen trioxide conformations corresponding to the maximum, minimum or saddlepoint energies of the internal rotational potential. The definition of structural parameters is indicated.
another. Thus, to a first approximation the OOO angle in H$_2$O$_3$ will be 90°. To diminish lone pair repulsion between the O atoms, the free valences of the terminal O atoms point to the y direction. Hence, the OH bonds stand perpendicular to the OOO plane, being either on the same side or on opposite sides of the plane. A reduction of the H, H repulsion will lead to a preference of the (og, og) conformation (see Fig. 2). Those forms with two vicinal lone pairs in the same plane and the third in a plane perpendicular to the first one will be less favorable. Again, one can distinguish between a form with favorably low H, H repulsion, namely the (ap, +og) conformation, and one with higher H, H repulsion, namely the (sp, +og) conformation. A maximum of electron repulsion can be expected for those forms which have all oxygen lone pair orbitals perpendicular to the plane of the oxygen atoms. In this case, the energies will increase from the (ap, ap) to the (sp, sp) form according to a parallel increase of H, H repulsion.

With the aid of the simple bonding model used above, the relative stabilities listed in Table I are reproduced in a qualitative way. In order to understand the structural details of H$_2$O$_3$, the perturbational molecular orbital (PMO) theory is adopted. The PMO analysis of H$_2$O$_3$ involves a dissection of the molecule into component fragments, then, the construction of group orbitals (GO) for each fragment and, finally, an examination of the key GO interactions which arise in the recombination process of the fragments. Hydrogen trioxide can be dissected into two fragments, namely OH and OOH. In turn, the OOH fragment can be further dissected into O and a second OH group. Thus, there are two fragmentation modes and two sets of fragmentation orbitals upon which the PMO analysis can be based. Those group orbitals which are of primary interest for a dissection into O and the (OH)$_2$ group are schematically shown in Fig. 3. Recalling that the magnitude of the stabilizing or destabilizing GO interactions is largely determined by the size of the overlap we compare the interactions $p_s(O) - \pi_x$, $p_s(O) - \pi_y$, and $p_s(O) - \pi_z$. Two of them, namely $p_s(O) - \pi_x$ and $p_s(O) - \pi_y$, can be excluded from the analysis because of zero overlap in all conformations. In a planar conformation, the interaction $p_s(O) - \pi_x$ will be destabilizing since two filled GO's interact. However, if the OH groups rotate, the destabilizing interaction of the overlap is reduced until it completely vanishes in an orthogonal conformation. Also, a stabilizing two electron interaction is possible between $p_s(O)$ and $\pi_z$ in the orthogonal conformation but not in the planar H$_2$O$_3$ forms. Hence, the conformational preference of skewd H$_2$O$_3$ forms over planar forms is accounted for by the PMO approach. Furthermore, it predicts shorter OO bond lengths for the orthogonal forms due to the additional overlap.

A similar result is obtained if the PMO analysis starts from a dissection into OOH and OH fragments. In Fig. 4, the GO's of hydroperoxyl and hydroxyl are depicted. They have been constructed from the corresponding H$_2$O$_3$ and H$_2$O MO's by removing the 1s contributions of one H atom. The double-head arrows, also drawn in Fig. 4, indicate those orbital interactions which become stabilizing $(\phi_4 - \phi_6, \phi_7 - \phi_4, \phi_7 - \phi_3, \phi_3 - \phi_7, \phi_7 - \phi_5)$ or less destabilizing $(\phi_3 - \phi_4)$ if the OH bond rotates out of the plane of the hydroperoxyl fragment. Additional stabilization of a (sp, +og) or (ap, +og) form of H$_2$O$_3$ can result from interactions $(\phi_7 - \phi_3, \phi_4 - \phi_5)$ where positive overlap between the $p_s$ orbital of the central O atom and the 1s orbital of the hydroxyl hydrogen are possible. Besides a shorter OOH bond length, a somewhat smaller OOH bond angle can be expected for the skewed forms.

Within the PMO approach, a distinction between the three planar forms is much more cumbersome since it requires reasonable estimates of overlap integrals and orbital energies for the analysis of almost a dozen possible interactions. Therefore, we refrain from a detailed PMO treatment, but utilize what is known from the quantum chemical study of hydrogen peroxide. For example, the charge distribution in H$_2$O$_3$ indicates that the large electronegativity of the oxygen atom gives rise to a considerable bond dipole moment which is directed from the H atom (positive end) to the O atom (negative

FIG. 2. Prediction of the most stable conformation of hydrogen trioxide by means of a simple bonding model.

FIG. 3. Group orbitals which result from a dissection of H$_2$O$_3$ into O and (OH)$_2$. Stabilization of the orthogonal conformations arises from the interactions indicated by double-head arrows.
In Eq. (1) the magnitude of the dipoles true for the (sp, sp) and the (ap, ap) conformation, but the distance \( r_{\text{ab}} \) is relatively small and the difference \( \tau_a - \tau_b \) vanishes. The latter is true for the (sp, sp) and the (ap, ap) conformation, but not for the (sp, ap) conformation \((\tau_a - \tau_b = 180°)\). The value of \( r_{\text{ab}} \) increases in the series (sp, sp), (sp, ap) and (ap, ap). Hence, the dipole–dipole interaction is highly unfavorable for the (sp, sp) form while the two other planar forms should be less destabilized, with the (sp, ap) form probably being slightly favored with regard to the (ap, ap) form. The destabilizing dipole–dipole interaction is further lowered if the OH bonds rotate in the \((\sigma_c, \sigma_c), (\sigma_g, \sigma_g)\) or \((\sigma_c, \sigma_g)\) positions, thus enlarging the values of the difference \( \tau_a - \tau_b \) and of the distance \( r_{\text{ab}} \). Compared with these conformations, the \((\sigma_c, \sigma_c), (\sigma_g, \sigma_g)\) and \((\sigma_c, \sigma_g)\) forms should be less favorable because of lower values of \( r_{\text{ab}} \) and \( \tau_a - \tau_b \). Similarly, one can predict that the (ap, ap) form is more stable than the (sp, ap) form because the latter should imply a larger dipole–dipole interaction.

The application of Eq. (1) not only leads to a relative ordering of conformational energies, but also explains the more open structures of those \( \text{H}_2\text{O}_3 \) forms with strong dipole–dipole interactions. However, the variations in the \( \sigma_\text{OO} \) bond lengths during rotation can be better described by a second quantum chemical effect, namely the tendency of lone pair electrons to delocalize in an adjacent polar bond. This effect was first described by Altona et al. and later formulated in a more general way by Pople and co-workers. It should cause a decrease of the \( \sigma_\text{OO} \) bond length if the lone pair orbital of a terminal O atom is co-planar with the bond between the two other O atoms. This can happen in the orthogonal conformations, thus underlining the stability of these forms.

Usually, one refers to a third effect in order to analyze the behavior of alicyclic rotors. This is the concept of bond staggering which is also applied to molecules with lone pair electrons. The latter are thought to be localized in \( sp^3 \) hybrid orbitals. Hence, rotational angles of 60° and 180° are the basic requirement for minimum lone pair repulsion and optimum \( \sigma_\text{OO} \) bond staggering.

The computed energies and structures do not support this argument. At all calculational levels, the \( \text{H}_2\text{O}_3 \) conformations of low energy (GMIN and LMIN) are characterized by rotational angles close to 90°. Although the deviations from the perfectly orthogonal positions of the \( \sigma_\text{OO} \) bonds, especially in the saddlepoint conformations, may arise from the tendency of lone pair staggering, this effect is certainly far less important than dipole–dipole interactions and lone pair delocalization.

**IV. COMPARISON WITH \( \text{H}_2\text{O}_3 \)**

The theoretical energies and conformations of \( \text{H}_2\text{O}_3 \) listed in Tables I and II reveal its close relationship to hydrogen peroxide. Despite the similarity of structural and conformational parameters, there exist some differences:

1. The \( \sigma_\text{OO} \) bond lengths of \( \text{H}_2\text{O}_3 \) are shorter than that of \( \text{H}_2\text{O}_3 \) by 1–2 pm depending on the conformation considered. In the orthogonal conformations, lone pair delocalization into an \( \sigma_\text{OO} \) bond is certainly more effective than into an \( \sigma_\text{OO} \) bond. This becomes fairly obvious if Altona’s interpretation of this effect is adopted which is based on the mixing of one oxygen \( \rho \) orbital with the suitably oriented \( \sigma_\text{OO} \) orbital of the \( \text{O} \) bond \((X = O \text{ or } H)\). As the \( \sigma_\text{OH} \) orbital is usually higher in energy than the \( \sigma_\text{OO} \) orbital, orbital mixing will be more pronounced in

![FIG. 4. The interaction of OOH and OH group orbitals in hydrogen trioxide. Interactions which become stabilizing or less destabilizing in a skewed position of the OH group are indicated by double-head arrows.](image1)

![FIG. 5. The interaction of the two OH dipole moments in \( \text{H}_2\text{O}_3 \). The symbols refer to Eq. (1).](image2)
H$_2$O$_2$ than in H$_2$O$_2$. The consequences of this effect can be observed in the OO bond lengths obtained for the saddlepoint conformations (Table II). There, only one OO bond strengthens while the other OO bond is weakened due to the stronger participation of its $\sigma^*$ orbital in the bonding process. As this weakening is not counterbalanced by a similar effect involving the $\sigma^*$ orbital of the stabilized bond, the latter is shorter than those of the (+og, +og) form. Similarly, the longest OO bonds are found for the saddlepoint conformations rather than for the planar forms as one could expect.

(2) While the lone pair orbitals of the terminal oxygen atoms are mainly involved in an interaction with the $\sigma^*$ orbital of the vicinal OO bond, those of the central O atom can interact with the OH bond, provided the lone pair orbital and the OH bond are coplanar. Again, this leads to a decrease of the corresponding OO bond and an increase of the OH bond length. It is not immediately clear why this effect should be larger for H$_2$O$_2$ than for H$_2$O as suggested by the $R$(OH) values of 95.3 pm (H$_2$O at equilibrium; RHF/basis C) and 94.6 pm (H$_2$O at equilibrium, RHF/basis C). However, the equilibrium dihedral angles of 116° (H$_2$O) and 80° (H$_2$O$_2$) indicate that the interaction of an O lone pair orbital with the OH bond is stronger for H$_2$O$_2$ because of geometrical reasons. Consequently, the OH bond lengths of H$_2$O$_2$ and H$_2$O are almost the same for the planar forms where this effect should play no significant role.

(3) Comparing the relative energies of H$_2$O$_2$ and H$_2$O, it becomes obvious that the barrier heights to internal rotation are not so strongly related as one could expect. The energy required to rotate H$_2$O$_2$ from the equilibrium conformation in the syn form is about 9 kcal/mole (RHF/basis C). A similar conformational process, namely (og, og) → (sp, sp), requires about 7 kcal/mole if the same level of RHF accuracy is used. The difference of 2 kcal/mole is rather low if one recalls the interactions between different pairs of atoms (H ... H vs H ... O) and different bonds (OH and (H vs OH and OO) for H$_2$O$_2$ and H$_2$O. Another 15 kcal/mole are necessary to bring H$_2$O$_2$ to the (sp, sp) conformation where the large increase may result from strong H, H repulsion. However, if one analyzes the electron distribution in the (sp, sp) form with the aid of the Mulliken population values, it becomes obvious that the interaction between the H atoms is attractive, rather than repulsive. While the H, H overlap population is negligible or even antibonding in all other conformations, significant bonding overlap characterizes the (sp, sp) form. This suggests the same kind of "aromatic" stabilization due to $\sigma$-electron delocalization which was found for singlet dimethylcarbene. Considering the atomic orbitals involved in the OH bond as well as the in-plane lone pair orbital of the central O atom, then, a ring of five atomic orbitals can be formed which is closed by the H, H interaction. The assignment of six $\sigma$-electrons to the three resulting bonding MO's will lead to some stabilization of the syn-periplanar arrangement displayed in the positive H, H overlap population.

The $\sigma$-effect is partially offset by a destabilizing $\pi$-effect. Similar to the situation in the allyl anion, the planar H$_2$O$_2$ molecule possesses three $\pi$ molecular orbitals, bonding, nonbonding, and antibonding. Since six electrons occupy these MO's, the net effect leads to slightly destabilizing interactions between the O atoms according to the computed $\pi$ overlap populations. Additional destabilization, of course, results from highly unfavorable dipole–dipole interactions.

The energy which is necessary to rotate one OH bond from the orthogonal position in the antiperiplanar position amounts to 5 kcal/mole. It doubles if the second OH bond is brought in the same position. Since the same process for H$_2$O$_2$ takes less than 1 kcal/mole (RHF/basis C) we can conclude that the trans arrangement of OO and OH bonds in H$_2$O$_2$ is less stable by more than 4 kcal/mole compared to H$_2$O$_2$. Probably, this is also caused by the unfavorable dipole–dipole interactions in the (ap, ap) and (ap, +og) forms of H$_2$O$_3$ which are not present in trans H$_2$O$_2$.

V. BASIS SET EFFECTS

The data compiled in Tables I and II indicate the basis set effects inherent in a RHF calculation of H$_2$O$_2$. In the case of H$_2$O$_2$ only augmented basis sets of the double-$\zeta$ quality lead to a trans barrier to internal rotation, i.e., small basis sets are insufficient to describe the stabilization of skewed H$_2$O$_2$ relative to its trans form. This is also true for H$_2$O$_2$ as the saddlepoint energy of S2 (Table I) increases by 2 kcal/mole from a minimal basis set calculation to an augmented basis set calculation. This basis set effect also occurs with other conformations of H$_2$O$_2$. For the all-trans arrangement of bonds in the (ap, ap) form, the increase of energy due to basis set enlargement is twice as large, namely 4 kcal/mole.

In contrast to H$_2$O$_2$, the energies of the syn-periplanar forms of H$_2$O$_3$ increase with an improvement of the basis. The increase amounts to 1 kcal/mole for the (sp, +og) conformation and 2 kcal/mole for the (sp, sp) conformation. Also, the basis set effects found for the (+og, -og) and (sp, ap) forms are in line with energy increases of 1 and 2 kcal/mole for rotation in a syn- or antiperiplanar form. We conclude that polarization functions are of similar importance for an accurate determination of the rotational barriers of H$_2$O$_2$ as they are for H$_2$O$_2$. With regard to the relative energies of the doubly augmented basis D, the same slight reduction of barrier heights exists as was found for H$_2$O$_2$.23

The actual basis set dependence is best found in the computed structures (Table II). The minimal STO-3G basis both underestimates the OO bond distances and overestimates the OH bond distances as a consequence of insufficient charge separation along the OH bond. Furthermore, the rigidity of the STO-3G basis leads to bond and dihedral angles close to 90°. Both effects contribute to the low cis and trans barriers obtained with the minimal basis A.

The structures obtained from basis set B show significant improvements. Due to its split valence shell character, basis set B gives a relatively large separation of charge in the OH bonds which is responsible for the increase of the OO bond lengths, the decrease of the OH...
D. Cremer: Hydrogen trioxide

TABLE III. Absolute and relative RS–MP energies of minima, maxima, and saddles of the conformational surface of H$_2$O$_3$. Numbers in parenthesis are second-order correlation energies.

<table>
<thead>
<tr>
<th>Point</th>
<th>Conformation (symmetry)</th>
<th>Basis B</th>
<th>Basis C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total energy (hartree)</td>
<td>(Corr. energy)</td>
<td>Total energy (hartree)</td>
</tr>
<tr>
<td>Absolute energies (hartree)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GMIN  + og, + og (C$_2$)</td>
<td>-225.62077 (-0.41421)</td>
<td>-226.09075 (-0.56513)</td>
<td></td>
</tr>
<tr>
<td>GMAX  sp, sp (C$_{3u}$)</td>
<td>-225.58952 (-0.41867)</td>
<td>-226.06486 (-0.56564)</td>
<td></td>
</tr>
<tr>
<td>LMIN  + og, - og (C$_2$)</td>
<td>-225.61327 (-0.41451)</td>
<td>-226.08511 (-0.56506)</td>
<td></td>
</tr>
<tr>
<td>LMAX1 ap, ap (C$_{3v}$)</td>
<td>-225.60637 (-0.41578)</td>
<td>-226.07235 (-0.56511)</td>
<td></td>
</tr>
<tr>
<td>LMAX2 sp, ap (C$_1$)</td>
<td>-225.60940 (-0.41067)</td>
<td>-226.07358 (-0.56511)</td>
<td></td>
</tr>
<tr>
<td>SI*  sp, + og (C$_1$)</td>
<td>-226.61295 (-0.41707)</td>
<td>-226.08044 (-0.56643)</td>
<td></td>
</tr>
<tr>
<td>S2*  + og, ap (C$_1$)</td>
<td>-226.61352 (-0.41472)</td>
<td>-226.08222 (-0.56540)</td>
<td></td>
</tr>
</tbody>
</table>

Relative energies (kcal/mole)

| Basis B | | | |
|--------|---------|---------|
| Absolute energies | | | |
| GMIN  + og, + og (C$_2$) | 0.0 (2.8) | 0.0 (0.8) |
| GMAX  sp, sp (C$_{3u}$) | 19.6 (0.0) | 22.5 (0.9) |
| LMIN  + og, - og (C$_2$) | 4.7 (2.6) | 6.5 (0.9) |
| LMAX1 ap, ap (C$_{3v}$) | 9.0 (1.8) | 11.5 (0.8) |
| LMAX2 sp, ap (C$_1$) | 7.1 (1.9) | 10.8 (0.8) |
| SI*  sp, + og (C$_1$) | 4.9 (1.0) | 6.5 (0.0) |
| S2*  + og, ap (C$_1$) | 4.5 (2.5) | 5.4 (0.6) |

*Saddlepoint energies have been approximated for basis B by setting $\delta_1(S1) = 0^\circ$ and $\delta_2(S2) = 180^\circ$, respectively, and optimizing the remaining geometrical parameters. In the case of basis C, the rotational angles have been taken from the Fourier analysis described in Sec. VII.

VI. CORRELATION EFFECTS

In order to get an estimate of the correlation error we have repeated calculations with basis B and C at the RS–MP level of theory. RS–MP total energies, second order correlation energies, intra- and interpair contributions as well as computed structures are summarized in Tables III, IV, and V. While the basis B barriers are slightly reduced with respect to the RHF values the contrary is true for the basis C barriers. The latter is consistent with the increase of barrier heights found for H$_2$O$_3$ at the RS–MP level. This increase results from a redistribution of charge from inner to outer shell regions due to the introduction of electron correlation. As a consequence, charge repulsion effects are somewhat larger, thus, leading to the higher barriers. It is interesting to note that the relative contributions of second order energies are about 1 kcal/mole smaller at the level of basis C than at level of basis B. Obviously, the observation that correlation contributions to the H$_2$O$_3$ barriers become negligible if the basis set approaches the HF limit, also holds for H$_2$O$_3$.

In contrast to the total correlation energies, the intra- and interpair portions (Table IV) significantly contribute to the relative conformational energies. The interpair correlation energy stabilizes the orthogonal forms while the intrapair energies favor the planar H$_2$O$_3$ conformations. Using the actual form of the molecular orbitals and the calculated electron distribution, it can be deduced that the lone pair MO’s of the orthogonal conformations span nearly the whole region of the molecule. Therefore, the interaction of the lone pairs and the bond pairs is large which is in line with the predictions of the PMO treatment of H$_2$O$_3$. However, in the planar forms, the lone pair MO’s do not span as much of the molecule. Hence, interpair interactions become less important while intrapair correlations become significant. The small net effect of the correlation energies on the barriers results from the well-balanced contributions of inter- and intrapair terms. As a consequence, the relative conformational energies of H$_2$O$_3$ can be determined at the HF level of theory with a reasonable degree of ac-

TABLE IV. Intra- and interpair energies of H$_2$O$_3$ obtained with basis C at the RS–MP level of theory. Absolute energies are given in hartree, relative energies (in parenthesis) in kcal/mole.

<table>
<thead>
<tr>
<th>Point</th>
<th>Conformation</th>
<th>Intrapair energy</th>
<th>Interpair energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>GMIN</td>
<td>+ og, + og (C$_2$)</td>
<td>-0.08360 (6.1)</td>
<td>-0.48154 (0.2)</td>
</tr>
<tr>
<td>GMAX</td>
<td>sp, sp (C$_{3u}$)</td>
<td>-0.09213 (0.7)</td>
<td>-0.47351 (5.3)</td>
</tr>
<tr>
<td>LMIN</td>
<td>+ og, - og (C$_2$)</td>
<td>-0.08316 (6.4)</td>
<td>-0.48190 (0.0)</td>
</tr>
<tr>
<td>LMAX1</td>
<td>ap, ap (C$_{3v}$)</td>
<td>-0.08749 (3.6)</td>
<td>-0.47763 (2.7)</td>
</tr>
<tr>
<td>LMAX2</td>
<td>sp, ap (C$_1$)</td>
<td>-0.09351 (0.0)</td>
<td>-0.47179 (6.3)</td>
</tr>
<tr>
<td>SI</td>
<td>sp, + og (C$_1$)</td>
<td>-0.09015 (2.0)</td>
<td>-0.47628 (5.3)</td>
</tr>
<tr>
<td>S2</td>
<td>+ og, ap (C$_1$)</td>
<td>-0.09033 (1.9)</td>
<td>-0.47507 (4.2)</td>
</tr>
</tbody>
</table>
curacy. Although this finding is in line with similar observations made for H$_2$O$_2$, it does not necessarily suggest that the relative interpair and intrapair contributions always cancel.

Unlike the barrier values, the computed RS–MP equilibrium structures of the seven H$_2$O$_3$ conformations (Table V) clearly differ from the corresponding RHF results. For both basis B and basis C, the bond distances become longer while the bond angles are slightly reduced. The RS–MP method uses all doubly substituted determinants $\Phi_{ij}^{0}$ in the calculation of the second order energy $\Delta E$ including double excitations from OO or OH bonding to OO or OH antibonding molecular orbitals. This allows for left–right correlation of the bond electrons. The corresponding contributions to the correlation energy are significant if the basis set provides low-lying virtual orbitals with the right nodal properties in the bond region. For basis B, these conditions are not fulfilled. Only, if the bond lengths are substantially increased from their HF values, is the gap between bonding and antibonding OO and OH MO's diminished and the contributions to the correlation energy arising from double excitations to $\sigma^{+}_{00}$, $\sigma^{0}_{00}$, and $\sigma^{+}_{0h}$ MO's become significant. Furthermore, the tendency of basis B to overestimate bond polarities influences the values of $R(OO)$ and $R(OH)$. As was already described for H$_2$O$_2$,$^{23}$ the inclusion of correlation effects causes a redistribution of charge from inner atomic to outer atomic regions. Consequently, charge repulsion is increased, thus leading to unreasonably long bond lengths of H$_2$O$_2$. To get reliable structural values an augmented basis like C is necessary which allows for sufficient left–right correlation of bond electrons. Any larger basis set than C should lead to a slight reduction of the bond lengths of Table V due to enhanced overlap. Especially, the $R(OH)$ values should decrease as basis C does not include polarization functions on the hydrogens.

In order to give some verification for these predictions we have augmented basis C with three p GTF's for hydrogen$^{24}$ and have repeated the structure optimization of the conformation of lowest energy at the RS–MP level. The energy thus obtained amounts to $-226.11275$ hartree including a second order correlation energy of $-0.57421$ hartree. The theoretical equilibrium parameters are: $R(OO)=143.9$ pm, $R(OH)=97.2$ pm, $\sigma(OOO)=106.3^\circ$, $\beta(HOO)=102.8^\circ$, and $\theta=78.1^\circ$. It may be noted that the calculated value of $R(OH)$ fits nicely in the series of theoretical OH bond lengths of H$_2$O (95.7 pm), H$_2$O$_2$ (96.7 pm), and HOF (97.2 pm) evaluated at the same level of accuracy.$^{30}$

### VII. THE INTERNAL ROTATIONAL POTENTIAL

Since the principal aim of this work is the investigation of the internal rotational potential surface of H$_2$O$_3$, we have calculated the analytical form of $E(\theta_1, \theta_2)$. For this purpose, a 60° grid was used covering the range $-180^\circ \leq \theta_1, \theta_2 \leq +180^\circ$. At each point, all bond lengths and bond angles have been optimized. In a first set of calculations, basis C was employed at the HF level of theory. Then, in a second set of calculations, the same conformations have been recalculated using basis C at the RS–MP level of theory. Again, all structural parameters have been optimized in order to get reliable predictions on correlation dependent changes of the conformational potential. The energies obtained in this way are listed in Table VI. The energy of GMIN is used as a reference, throughout.

be reasonably approximated by the truncated Fourier expansion (2):

$$V(\theta) = \sum_{k=0}^{n} (V_k^c \cos k\theta + V_k^s \sin k\theta),$$

where $m$ takes a finite value. The decomposition of the potential $V$ into its Fourier components $V_k$ facilitates the interpretation of the rotational barriers as has been shown by Radom et al. \(^{28}\) The success of this approach makes it desirable to develop the potential of a multi rotor in a similar way. In the case of $\text{H}_2\text{O}_3$, the dependence of $V$ on the rotational angles $\theta_1$ and $\theta_2$ can be written as

$$V(\theta_1, \theta_2) = \sum_{k=0}^{n} \sum_{l=0}^{n} (V_{kl}^c \cos k\theta_1 \cos l\theta_2 + V_{kl}^s \cos k\theta_1 \sin l\theta_2 + V_{kl}^t \sin k\theta_1 \cos l\theta_2 + V_{kl}^u \sin k\theta_1 \sin l\theta_2).$$

(3)

In order to reduce the numerous terms in Eq. (3) the summation limits $m = n = 3$ are chosen in accordance with the treatment of single rotors. Furthermore, all Fourier terms can be excluded which do not comply with the $C_{3v}$ symmetry of the potential surface. The remaining terms have been systematically investigated by performing a least-squares analysis for a series of trial expansions of Eq. (3) using a total of 19 $ab$ initio energies. According to the evaluated standard deviations $\sigma$ and correlation coefficients $r^2$, \(^{31}\) the best fit of the $ab$ initio data has been achieved with Fourier expansion (4)\(^{32}\):
As in the case of a single rotor, the magnitude of the $V_{90}$ terms illustrates the relative importance of dipole, hyperconjugative and bond staggering effect. According to the values of columns 1 and 2 of Table VII, the first and the second effect dominate the form of the potential while the influence of bond staggering is moderate. A similar observation can be made for the cross terms $V_{91}$, which describe the coupling of the three electronic effects. Fourier coefficients like $V_{31}$ or $V_{40}$ have been found negligible in all trial calculations, also indicating the reduced importance of bond staggering. On the other hand, the values of $V_{11}, V_{20}$, and $V_{10}$ are considerable arising from the influence of the dipole–dipole interactions, from the coupling between the hyperconjugative effects, and from the coupling between dipole and hyperconjugative effect. Since the interaction energy of two dipoles is proportional to $\cos(\tau_k - \tau_l)$ (see Eq. (1)) it seems reasonable to include a $\cos(\theta_1 + \theta_2)$ term in the Fourier expansion where the positive sign in the cosine argument results from the different definitions of $\tau_k$ and $\theta_2$ (see Figs. 1 and 5). However, the angle $\omega_5$ as well as the values of $\mu_4$ and $\mu_5$, and the distance $r_{45}$ also vary with the rotational angles $\theta_1$ and $\theta_2$, thus leading to a more complicated dependence of the dipole–dipole interaction energy on $\theta_1$ and $\theta_2$ than that which is provided by a single cosine term. Therefore the cosine and sine part of the $\cos(\theta_1 + \theta_2)$ are separated in Eq. (4) to improve the description of the rotational potential.\textsuperscript{33}

The positive sign of $V_{11}^\alpha$ indicates that the $(sp, ap)$ conformation is more stable than the other planar forms while the negative sign of $V_{11}^\beta$ indicates the preference of the $(og, og)$ forms over the $(og, -og)$ forms. The main features of the potential are reflected by the terms $V_{10}, V_{20}$, and $V_{11}$ while second order effects which decide on the exact energies and locations of minima and saddlepoints can be extracted from the remaining terms of Eq. (4). The $V_{11}^\beta$ term, for example, leads to a stabilization of the saddlepoint conformations relative to the planar forms. Their location outside the 1st and 3rd but inside the 2nd and 4th quadrant of the $\theta_1, \theta_2$ coordinate system has to do with the negative sign of $V_{11}^\beta$ which also plays a role with regard to the position of GMIN and LMIN. An interplay of the negative $V_{11}^\beta$, the negative $V_{20}$, and the positive $V_{12}$ causes a shift of GMIN to $\theta$ values lower than 90° because all these terms favor the $(sc, sc)$ forms. As for LMIN, these effects neutralize since $V_{11}^\beta$ stabilizes conformations close to $\theta_1 = \theta_2 = 135°$ which are destabilized by the $V_{20}$ and $V_{12}$ term.

Although none of the $V_{12}$ or $V_{11}$ terms of Eq. (3) complies with the symmetry restriction on $V(\theta_1, \theta_2)$, the inclusion of a cross term $V_{12}$ proved to be necessary to give a satisfactory fit of the \textit{ab initio} energies. It turned out that among the linear combinations of $V_{12}$ terms with the right symmetry, the terms $(V_{12}^\alpha + V_{12}^\beta)$ and $- (V_{12}^\alpha + V_{12}^\beta)$ are most important where the sine part provides an efficient differentiation between the $C_6$ and $C_2$ conformations of H$_2$O$_3$.\textsuperscript{33} Without loss of accuracy, the two $V_{12}$ components can be contracted to give the last term of Eq. (4).

Using the Fourier expansion $V(\theta_1, \theta_2)$, energy contour maps of the internal rotational potential of H$_2$O$_3$ have been plotted. The RS–MP rotational surface is shown in Fig. 6. One-dimensional sections out of this surface for $\theta_1 = 0°, 60°, 120°$, and $180°$ are displayed in Fig. 7. Both plots reflect the coupling between the OH rotors which is strongest for small rotational angles. For regions close to $180°$, there appears to be some decoupling indicating similar dipole–dipole interactions for $C_6$ and $C_2$ conformations that are almost planar.

Before discussing Fig. 6 in more detail, we would like to stress the correspondence between RHF and RS–MP Fourier coefficients (columns 1 and 2, Table VII). As was shown in Sec. VI, correlation effects change only slightly the barrier values due to the cancellation of intra- and interpair contributions. Surprisingly, it turns out that this conclusion also holds for the complete conformational potential. Contour maps of the intra- and interpair portions of the correlation energy shown in Figs. 8 and 9 are nearly the negatives of each. The form of the contours are almost identical in both plots, except that the maxima of the intrapair energies correspond to the minima of the interpair energies and vice versa. The location of these points is in line with our observation that the planar forms are stabilized by the intrapair contributions while the $(og, og)$ and $(og, -og)$ conformations are favored by the interpair contributions. Their net effect widely cancels giving rise to correlation contributions to the potential of 1–2 kcal/mole as shown in the contour map of relative correlation energies in Fig. 10. Although these values may decrease further with an improvement of the basis, two points can be made with regard to the dependence of correlation effects on the rotational angles. First, correlation effects are strongly coupled to $\theta_1$ and $\theta_2$. Secondly, the

\[ \text{J. Chem. Phys., Vol. 69, No. 10, 15 November 1978} \]
variation of the correlation energy is largest for conformational changes which preserve $C_2$ symmetry, i.e., along the left–right diagonal of Fig. 10, while it is relatively low for an internal rotation which preserves $C_1$ symmetry, i.e., along the right–left diagonal. This is in line with the observation already made for the total energies of $H_2O_3$ and confirms that the electron rearrangement is more drastic for the symmetry retaining inversion of the (og, og) form than for the corresponding inversion of the (+og, -og) form.

FIG. 7. Sections, $V(\theta_1)$, out of the potential surface for internal rotation of hydrogen trioxide for fixed values of $\theta_1$. The dashed lines show the energy variation along the flip-flop rotational paths. They have been calculated by choosing polar coordinate systems centered at GMAX and LMAX1. The corresponding phase angles are defined to be 0° or 180° for the points GMIN and 90° or 270° for the points LMIN.

VIII. THE FLIP-FLOP ROTATION OF THE DOUBLE ROTOR

With the aid of the energy contour map of $H_2O_3$, various rotational modes can be discussed. Synchronous rotation of both OH groups of the stable (og, og) form, either disrotatory or conrotatory, are prohibited by the large barriers at GMAX, LMAX1, and LMAX2. The two step rotations which are indicated by the dashed lines in Fig. 6 are more probable. They surround the con-

FIG. 8. The intrapair energies of hydrogen trioxide as a function of $\theta_1$ and $\theta_2$. Contours indicate kcal/mole above the intrapair energy of LMAX2.

FIG. 9. The interpair energies of hydrogen trioxide as a function of $\theta_1$ and $\theta_2$. Contours indicate kcal/mole above the interpair energy of the (se, se) conformation of $H_2O_3$. 

At this point, it is interesting to compare the internal rotation of the double rotor H$_2$O$_3$ with the conformational processes possible in five membered rings. As one can see from Fig. 11 the H$_2$O$_3$ conformations lying in the -90° < $\theta_1$, $\theta_2$ < 90° section of the $\theta_1$, $\theta_2$ surface are related to certain ring conformations. For example, the (sp,sp) form is equivalent to the planar five membered ring, the (+og, -og) form to the envelope form, and the (+og, og) form to the twist form. Correspondingly, the inversion of the twist conformation of the ring can be compared with the synchronous disrotatory (inward) rotation of the (og, og) form of H$_2$O$_3$. The other conformational process found for five membered rings, namely pseudorotation, resembles the flip-flop rotational mode of H$_2$O$_3$. This relationship is illustrated in Fig. 11 where various H$_2$O$_3$ conformations are drawn in a way to represent a five membered ring pseudorotating from one (og, -og) form to the other.

It is known that pseudorotation is energetically more favorable than an inversion of the ring. This has to do with the fact that during pseudorotation ring bonds, internal ring angles, and torsional angles periodically vary within certain limits with a phase shift of $\pi$/5 while the inversion process causes a simultaneous change of all parameters taking extreme values in the planar form. We have investigated whether a similar connection applies to the rotational modes of H$_2$O$_3$. In Fig. 12, a contour map of the OO angle $\alpha$ of H$_2$O$_3$ is shown. The paths for the flip-flop rotations have been transferred from Fig. 6. Similar plots for the OO bond angles and the OO bond lengths are given in Figs. 13 and 14. Bond angles and OO bond lengths are coupled to a large degree with the torsional angles $\theta_1$ and $\theta_2$. The contour maps nicely reflect the influence of the two dominating electronic factors. The variation of the bond angles occur in parallel with the changes of the dipole–dipole interactions. This is illustrated by both the direction of the central contour ellipses and the angle minimum in the vicinity of GMIN. The contour map of the OO bond lengths is characterized by a twofold periodicity indicating that the variations of R(OO) are mainly caused by the hyperconjugative effect.

In view of the coupling between structural parameters and rotational angles, the predictions of a rigid rotor...
model seem problematic. However, if one considers only the flip-flop rotational path corresponding to the pseudorotation of a five membered ring, the rigid rotor model has some justification. The variations of the bond angles along the dashed line encircling GMAX amount to less than $2^\circ$ while those along the “inversion” path (synchronous rotation through the (sp,sp) form) are about four times larger. The OO bonds vary between 144 and 148 pm for both rotational processes. During the flip-flop rotation at least one OO bond length is strengthened. However, the inversion process involves conformations with two unfavorably long OO bond distances. These findings are consistent with the observations made for pseudorotation and stress the relationship of the conformational processes of a geminal double rotor and a five membered ring.

This relationship suggests using the $\theta_1, \theta_2$ surface of H$_2$O$_3$ for qualitative predictions concerning the conformational tendencies of 1,2,3-trioxolanes. Apart from the fact that the hydrogens in H$_2$O$_3$ are replaced by a CH$_2$-CH$_2$ bridge and, hence, the bond polarities are slightly changed, it seems reasonable to expect similar electronic effects for both compounds. At first sight, the twist form of the trioxolane appears to be the conformation of lowest energy since it corresponds to the (sc,sc) form of H$_2$O$_3$. This conclusion has also been drawn by Blint and Newton. A more detailed analysis of the situation is necessary if one recalls that the torsional angles of a puckered five membered ring are considerably smaller than $90^\circ$, varying from $0^\circ$ to $40^\circ$ around the ring. In the twist ($C_2$) conformation, the angles $\theta_1$ and $\theta_2$ of the OOO moiety are rather small since the main torsion is around the CC bond. The reverse situation applies to the envelope ($C_3$) form of 1,2,3-trioxolane. According to inspection of the model, torsional angles $\theta$ of about $10^\circ$ and about $40^\circ$ seem appropriate for the twist and the envelope forms. Inserting these angle values in the $V(\theta_1, \theta_2)$ potential of H$_2$O$_3$ it becomes obvious that the twist form should be less favorable than the envelope form of 1,2,3-trioxolane. The stabilization of the latter is predicted to amount to 6-7 kcal/mole. Probably, this energy differ-

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**FIG. 12.** The variation of the OOO bond angle $\alpha$ as a function of the rotational angles $\theta_1$ and $\theta_2$. Contours are given in degrees. The dashed lines are transferred from Fig. 6.

**FIG. 13.** The variation of the OOH bond angle $\beta$ as a function of the rotational angles $\theta_1$ and $\theta_2$. Contours are given in degrees. The dashed lines are transferred from Fig. 6.

**FIG. 14.** The variation of the OO bond length as a function of $\theta_1$ and $\theta_2$. Contours are given in picometers. The dashed lines are transferred from Fig. 6.
ence will be reduced by ~3 kcal/mole because of unfavor-
orable methylene group eclipsing in the envelope form. Consequently, we predict the envelope form to populate the minima of the conformational surface of 1,2,3-tri-
oxolane which should be characterized by a barrier to pseudorotation of 3–4 kcal/mole. An inversion of the envelope form should require about 7 kcal/mole deduced from the energies of the (sp,sp) form of H2O3 (22 kcal/
mole) and a skewed form of H2O3 (~15 kcal/mole for \( \theta_1 = - \theta_2 = 45^\circ \)). As these predictions are at variance with the calculations of various other authors, a computational verification will be given in the third paper of this series.

IX. H2O3—A PROTOTYPE FOR GEMINAL DOUBLE ROTORS

Considering H2O3 as a prototype for geminal double rotors one can expect a similar rotational behavior for molecules of the type X(OY)2. In order to verify this assumption we have taken the results of theoretical studies of the internal rotational surface of methanol16,19 (X = CH3, Y = H), dimethoxymethane18 (X = CH3, Y = CH3), the phosphate anion40 (X = PO3, Y = H), and the dimethyl phosphate anion51 (X = PO3, Y = CH3) from the recent literature. A fit of the conformational energies of these molecules to the Fourier expansion (4) leads to the \( V_{4t} \) coeffi-
cients listed in Table VII.

According to the computed standard deviations and correlation coefficients, the internal rotational potential of all these molecules is satisfactorily described by expansion (4). The best fit is obtained for the H2PO4 molecule for which we calculate small or vanishing cou-
pling terms \( V_{11} \), \( V_{22} \), and \( V_{12} \). Also, a low dipole effect and a reduced hyperconjugative effect is signified by the values of \( V_{10} \) and \( V_{20} \). This finding can be explained by the negative charge associated with the PO4 group of the molecule. It opposes the electron withdrawal from the H atoms, thus reducing the OH dipole moments independently from their rotational positions. Accordingly, the dipole–dipole interactions do not play the important role as in the case of H2O3. The OH rotors are only weakly coupled which is illustrated by the nearly circular contours of the potential surface. Evidently, the small inter-
actions between the rotating groups explain the suc-
cess of Kollman’s attempt to describe the internal rotational potential of H2PO4 with a small Fourier expansion, including just one coupling term.40

For (CH3)2PO4, the dipole effect and the dipole–dipole interactions seem to have become larger. However, this increase can be caused by the rigid rotor model used for the double rotor.41 Steric repulsion will be exaggerated in the crowded conformations of the molecule, thus lead-
ing to undue charge separations. The large Fourier coef-
ficients of the rigid rotor potential of dimethoxymethane support this interpretation. Therefore, we refrain from a detailed discussion of these values.

In the case of the methanediol, the terms \( V_{10} \) and \( V_{11} \) nicely reflect the effects of the two basis sets. It is obvious that basis B leads to an exaggeration of the dipole effect which is in line with its tendency to overestimate bond polarities. Contrary to the other rotor molecules studied, the \( V_{10} \) coefficient is positive indicating a preference for a cis arrangement of bonds in the HO–CH2–O moiety over a trans arrangement. This is consistent with the assumption of two bond dipole moments both di-
rected towards the oxygen atoms, thus being opposed in the cis form and reinforcing each other in the trans form. Two other conclusions can be drawn from the internal rotational potential of CH3(OH)2. First, the hyper-
conjugative effect is rather small which suggests that the interaction between the \( s^*_p \) and \( p(O) \) orbitals is not as strong as the corresponding interaction found for H2O3. Secondly, the \( V_{30} \) term indicates that bond stag-
gering has become more important. The interplay of an increased value of \( V_{30} \) and the positive sign of \( V_{10} \) leads to a shift of the global minimum from the (og,og) form to the (sc,sc) form.

With the aid of the \( V_{4t} \) coefficients of Table VII and Eq. (4), we have calculated the exact locations and ener-
gies of the saddlepoints of the CH3(OH)2, CH3(OCH3)2, H2PO4 and (CH3)2PO4 conformational surface. Apart from dimethoxymethane where the available ab initio data are not sufficient to describe the complete \( \theta_1, \theta_2 \) potential, we find that the flip–flop rotation of the gemi-

nal double rotors proves to be the energetically favored conformational process. The computed barriers are 5.2 (S1, Basis B), 4.4 (S2, Basis B), 3.8 (S1, Basis C), and 3.4 kcal/mole (S2, Basis C) for methanol, 3.2 (S1) and 3.3 kcal/mole (S2) for the monophosphate anion, and 4.3 (S1) and 3.2 kcal/mole (S2) for the dimethyl phosphate anion. These barrier heights favorably com-
pete with those of single rotors and underline the con-
formational flexibility of the double rotors.

X. CONCLUSIONS

The principal conclusions of this work may be sum-
madized as follows:

(1) Accurate calculations on the conformational potential of H2O3 require the inclusion of polarization func-
tions in the basis set as well as a complete structure optimization. As in the case of the trans barrier of H2O3, an insufficient flexibility of the basis leads to an underestimation of the barriers to internal rotation by 1–2 kcal/mole.

(2) Correlation effects have only a small influence on the relative energies of H2O3, although the intrapair and interpair contributions vary considerably with the rotation angles. Their low net effect results from an almost complete cancellation over the whole range of the conformational surface which is nicely shown by Fig. 8 and Fig. 9. The influence of correlation decreases if the basis set is improved. Therefore, an accurate re-
cording of the conformational potential of hydrogen tri-
oxide is possible at the HF level of theory.

(3) On the other hand, the determination of the equi-
librium structure of H2O3 with the HF method appears to be problematic. If the split valence basis B is employed, reasonable structures are calculated. However, this re-
sult is fortuitous as it is caused by an overestimation of the bond polarities and an insufficient description of...
overlap. Calculations with the augmented basis C provide evidence that the HF method predicts an erroneous equilibrium structure characterized by short O-O bond lengths of \(~139\) pm. The inclusion of left-right correlation of electrons in the theoretical model turns out to be mandatory to get a reliable structure of H$_2$O$_3$. We note that polarization functions both for the oxygen and the hydrogen atoms become even more important at the RS-MP level than at the HF level of theory.

(4) The conformational behavior of H$_2$O$_3$ is dominated by the dipole and the hyperconjugative effect which have also been found to be important for H$_2$O$_2$. The relative stabilities of the various H$_2$O$_3$ forms can be qualitatively interpreted on the basis of these electronic effects. Their interplay determines the coupling between the OH rotors.

(5) The internal rotational potential is satisfactorily described by the Fourier expansion in Eq. (4). The various $V_{n\ell}$ terms used in Eq. (4) allow a detailed analysis of the dependence of the electronic effects on the rotational angles. In addition, this potential facilitates the exploration of the internal rotational surface and provides reasonable estimates of the location of the saddlepoints and the steepest descent paths connecting saddlepoint and minimum conformations.

(6) According to the computed energies, the most favorable conversional process of H$_2$O$_3$ corresponds to a two-step flip-flop rotation by which the molecules surrounds the energy maxima of the potential surface. We emphasize that the relative energies of the planar H$_2$O$_3$ conformations are completely misleading with regard to the rotational flexibility of the molecule. An accurate determination of the barriers to internal rotation of a double rotor demands explicit knowledge of the saddlepoint energies of the potential. In the case of hydrogen trioxide, the actual barriers (6.5 and 5.4 kcal/mole) represent only a fraction of the relative energies of the planar molecular forms which populate the maxima of the rotational surface.

(7) It has been shown that the flip-flop rotation of geminal double rotors is comparable to the pseudorotation of five membered rings. This relationship has been used to predict the conformational tendencies of 1,2,3-trioxolanes. Applying the calculated H$_2$O$_3$ potential, we expect the envelope form of the ring to be more stable by 3–4 kcal/mole than the twist form, the latter populating the barrier to pseudorotation. Our prediction is at variance with the results of various other quantum chemical investigations.

(8) We consider H$_2$O$_3$ to be a prototype for geminal double rotors of the type X(OY)$_2$. An analysis of the available \textit{ab initio} calculations on methanediol, dimethoxy methane, the monophosphate anion, and its dimethyl derivative supports our view.

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17. D. Cremer, (to be published).
18. W. J. Hehe, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana.
20. Similar conclusions can also be drawn if the electronic structure of ozone is considered. Ozone is a diradical with a weak r-bond between the two terminal atoms. (See, e.g., W. A. Goddard, III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Acc. Chem. Res. 6, 366 (1973)). Thus, the H atoms in H$_2$O$_3$ would be expected to be bonded on the terminal O atoms, in a plane perpendicular to the O$_2$ groups.
22. In the case of the interaction of a doubly occupied orbital $\sigma^*$ and a singly occupied orbital $\sigma(\text{or } \pi)$ it has been as-
assumed that the \( \pi \)-like overlap is smaller than 0.33. Under this condition, the interaction is stabilizing. See (a) R. F. Hudson, Angew. Chem. 85, 63 (1973); (b) F. Bernardi, N. D. Epiotis, W. Cherry, H. B. Schlegel, M-H. Whangbo, and S. Wolfe, J. Am. Chem. Soc. 96, 469 (1976).


24Equation (1), of course, represents the energy of interaction between two ideal dipoles \((\mathbf{r}_{ab} \gg 1)\) which significantly deviates from the value of (1) if real dipoles are considered \((\mathbf{r}_{ab} \sim 1)\). See, for example, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1964), Chap. 12.


29The structures of a variety of two and three-heavy atom molecules have been evaluated at the RHF and RS-MP level of theory with augmented basis sets. The RHF bond lengths are consistently found to be too short with regard to experimental values while the RS-MP values are in agreement with observed bond lengths. D. Cremer, (to be published).

30D. Cremer and D. Christen, J. Mol. Spectrosc. (submitted for publication).

31The standard deviation is defined by \( \sigma = \left( \frac{1}{N-M} \sum_{i=1}^{N} (E(\theta_1, \theta_3) - V(\theta_1, \theta_3))^2 / (N-M) \right)^{1/2} \) where \( \mathbf{V} \) ab initio energies are used to determine \( M \) Fourier coefficients \( V_M \). The square of the correlation coefficient \( r \) is given rather than \( r \) itself because \( r^2 \) provides a better descriptive measure.

32The form of the \( V_{ab} \) terms has been chosen according to the convention used for single rotors.

33The \( \cos(\theta_1 + \theta_2) \) term remains constant for \( \theta_1 = -\theta_2 \), but it varies for \( \theta_1 = \theta_2 \) which is appropriate since the largest change in energies occurs along the line \( \theta_1 = \theta_2 \). A dissection into a sine and a cosine part has the advantage that a variation of energies is induced along both diagonals. The same holds for the inclusion of the sine parts in the \( V_{12} \) term.

34There are only four \( S2 \) saddlepoints within the range \(-180^\circ \leq \theta_1, \theta_2 \leq 180^\circ \). (See values of \( \theta_1 \) and \( \theta_2 \) in Tables II and V.) The steepest ascent and descent paths to and from one of the eight saddlepoints have been calculated by means of Eq. (4).

35D. Cremer and J. A. Pople, J. Am. Chem. Soc. 97, 1358 (1975), and references cited therein.

36The dependence of \( R(\theta) \) and \( \beta(\theta) \) on \( \theta_1 \) and \( \theta_2 \) has been calculated with expansion (4) by decoupling the Fourier components combined in \( V_{10}, V_{20}, V_{30}, \) and \( V_{12} \).

37(a) J. Renard and S. Fliszár, J. Am. Chem. Soc. 92, 2629 (1970); (b) S. Fliszár, J. Renard, and D. Z. Simon, 93, 6853 (1971); (c) R. A. Rouse, 95, 3460 (1973).


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