Tetrahedron Vol. 35, pp. 1239 to 1245
0040-4020/79/0515-1239/$02.00/0

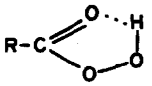
A THEORETICAL INVESTIGATION OF THE ROTATIONAL BARRIERS OF PEROXYFORMIC ACID

ROBERT D. BACH*, CARL L. WILLIS and TIMOTHY J. LANG
Department of Chemistry, Wayne State University, Detroit, MI 48202, U.S.A.

(*Received in USA* 2 *May* 1978)

Abstract—The internal rotational barriers in peroxyformic acid have been studied employing *ab initio* MO calculations. The C–O and O–O rotational barriers were calculated to be 7.68 and 1.04 kcal/mol, respectively. The relatively low O–O rotational barrier is attributed to a balance between electron repulsion and hydrogen bonding in the syn chelated conformer.

Peroxyacids have been utilized by organic chemists for many years. In particular, they have been used to prepare 1,2-epoxides which are useful synthetic intermediates.[1] The ground state structures of this important class of organic peroxides have not yet been fully elucidated.[2] IR studies have suggested that peroxyacids are H-bonded and monomeric in solution.[3,4] The insensitivity of this IR band to dilution is consistent with intramolecular H-bonding as depicted in 1. The OH stretching frequency (~3300 cm^{-1}) of peroxyformic acid remains essentially unchanged in going from the liquid to the vapor phase. Therefore, the H atom must presumably be in the same environment in both physical states. A valency force field analysis of performic and peracetic acid based upon IR data arrived at the same conclusion.[5] However, dipole moment studies in dilute solution suggested that peroxyacids are non-planar.[2,6,7] The planar structure 1 was deemed untenable by Swern[2,6] on the basis of his dipole moment studies. He proposed that the $-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-$ moiety was planar, but the –OH group was twisted out of the plane by an angle $\phi = 72° \pm 4°$ as in 2. X-ray crystal structure analyses of *o*-nitroperbenzoic acid[8a] and peroxypelargonic acid [8b] established the OCOO portion of the molecule to be essentially planar in the crystalline state. After some difficulty with data refinement, a dihedral angle between the COO and OOH planes of 146° was calculated.[8a] Their data suggested that the dihedral angle was determined by intermolecular H-bonding. It is not surprising that crystal forces in the solid state could outweight the electron repulsions of the O–O bond since the empirical values for the *trans* barrier of typical O–O bonds are between 0.32 kcal/mol (microwave) and 0.86 kcal/mol (IR).[8c] The inherent difficulty in purifying peracids, as well as their instability, has prevented a more detailed structural investigation of these compounds.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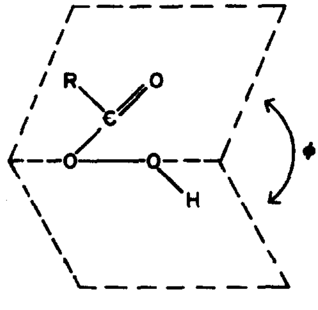

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Theoretical investigations of the structure of peracids have also been reported. Extended Huckel[9a] and *ab initio* (STO-3G)[10] calculations suggest that planar peracetic acid is more stable than a skewed conformation with rotation about the O–O bond (ϕ in 2). Semiempirical calculations of the charges and bond orders of an intramolecularly H-bonded peracid have also been reported.[9b] The planar structure of peroxyformic acid has also been calculated with an STO-2G basis set.[9c]

There have been relatively few attempts to determine the barrier to rotation about the O–O bond in a peracid. This is rather surprising since the internal rotation barrier of the O–O bond in hydrogen peroxide has been extensively studied.[11–14] Both *ab initio* (STO-3G) and semiempirical (PCILO) calculations[10] suggest that the O–O rotational barriers in peroxyacetic and peroxytrifluoroacetic acid are between three and four kcal/mol.

A second significant aspect of a theoretical study of peroxyacids is the effect of H-bonding on the equilibrium conformation and barrier to internal bond rotation. Recently, nonempirical calculations have been reported on various H-bonded systems.[15] The intramolecular H-bonding in formic acid has also been investigated by *ab initio* methods of calculation.[16] The calculations have been in good agreement with experimentally observed rotational barriers.

We now report our theoretical investigation of the structure and rotational barriers in peroxyformic acid. Our interest in this problem originated in a theoretical study of the mechanism of the epoxidation of alkenes by peracids.[17] A fundamental understanding of the origin and magnitude of the internal rotational barriers to be anticipated along the reaction coordinate for oxirane formation is vital to determining the overall mechanism of expxidation.

Method of calculation

Most of the INDO and STO-3G calculations were executed on an IBM 360/67 computer, while the more extensive 5-31G calculations were performed on an Amdahl Model 470V/6 computer. Each total energy calculation for peroxyformic acid required 1, 3.4, 32 and 32 min with INDO, STO-3G, 4-31G and 5-31G, respectively on the IBM. The 5-31G calculations required 2 min on the Amdahl computer.

The INDO calculations utilized the method described by Pople.[18] INDO calculations on peroxyformic acid used the reported X-ray geometry[22] for *o*-nitroperbenzoic acid, except that the molecule was assumed to be planar with a C–H bond distance of 1.10 A°. The *ab initio* calculations were carried out with the Gaussian 70 program with standard MO theory using the minimal STO-3G basis set for the O–O and C–O internal rotation, and the extended 5-31G Gaussian basis set for the final O–O rotational barrier.[19] Initial 5-31G calculations used the geometry obtained by minimization by STO-3G.The rotational barriers calculated by both STO-3G and 5-31G used geometries obtained by exhaustive minimization of *all bond angles and distances.*[20] The results of optimization of all bond distances to ±0.001 A° and bond angles to within ±0.1° are given in Table 1. The rotational barriers for the O–O and C–O bond in peroxyformic acid were plotted from calculations generated by altering the requisite dihedral angles, ϕ, by 30° increments between the limits of 0° and 180°. The calculated rotational barriers are presented in Figs. 1 and 2.

The STO-3G and 5-31G barriers to rotation about the O–O bond in peroxyformic acid were obtained by fitting the data obtained at 30° intervals to a truncated Fourier expansion of the form[21b]

$$E(\phi) - E(\phi_{\min}) = \sum_{k=1}^{6} V_k \frac{1 - \cos k\phi}{2} - V_0.$$

The terms $E(\phi) - E(\phi_{\min})$ represent the calculated

Table 1. Geometric parameters used for peroxyformic acid calculations

Rotation Angle (deg)	Bond Distances (Å)					Bond Angles (deg)					Dihedral Angles (deg)[a]	
	O-O	C-O	C=O	O-H	C-H	O-O-H	O-O-C	O-C=O	O-C-H	O=C-H	θ	ϕ
						X-ray Geometry						
	1.478	1.337	1.214	1.120	(1.100)	112.0	108.9	1.247	110.2	125.1		
	1.44	1.35	1.23				112	121.6	110.2	128.2		
						INDO[c]						
	1.24			1.05		104.0	106.0				0.0	0.0
						O-O Rotation STO-3G						
0	1.400	1.399	1.216	1.007	1.102	101.94	109.52	121.56	110.88	127.56	0.0	0.0
30	1.398	1.404	1.214	1.005	1.103	102.74	109.65	122.31	110.30	127.39	7.90	30.0
60	1.395	1.411	1.212	1.004	1.103	103.06	109.27	123.52	109.40	127.08	7.86	60.0
90	1.395	1.413	1.210	1.003	1.104	102.20	108.60	124.39	108.79	126.82	6.09	90.0
120	1.398	1.412	1.210	1.002	1.104	100.90	107.99	124.83	108.43	126.74	4.03	120.0
150	1.402	1.408	1.210	1.001	1.104	99.90	107.31	124.95	108.33	126.72	1.67	150.0
180	1.404	1.406	1.210	1.000	1.104	99.06	106.95	124.88	108.37	126.75	0.0	180.0
						5-31G						
0	1.452	1.350	1.204	0.9667	1.073	105.34	114.08	123.39	110.16	126.45	0.0	0.0
30	1.449	1.353	1.202	0.9645	1.074	105.53	113.96	123.75	109.83	126.42	7.98	30.0
60	1.443	1.360	1.198	0.9612	1.075	105.46	113.78	124.75	108.93	126.32	11.61	60.0
90	1.441	1.365	1.195	0.9591	1.076	104.23	113.55	125.86	108.00	126.14	10.73	90.0
120	1.444	1.365	1.193	0.9579	1.076	102.22	113.12	126.63	107.42	125.95	6.80	120.0
150	1.448	1.363	1.193	0.9577	1.077	100.49	112.47	126.75	107.36	125.89	2.63	150.0
180	1.450	1.361	1.193	0.9576	1.077	99.81	112.11	126.67	107.45	125.88	0.0	180.0
						C-O Rotation STO-3G						
0	1.404	1.406	1.210	1.000	1.104	99.06	106.95	124.88	108.37	126.75	0.0	180.0
30	1.406	1.413	1.211	1.000	1.105	99.15	106.54	124.47	109.50	126.03	30.0	180.0
60	1.409	1.426	1.211	1.000	1.106	99.23	105.31	123.32	111.93	124.75	60.0	180.0
90	1.411	1.432	1.211	1.000	1.106	99.30	104.10	122.21	113.51	124.28	90.0	180.0
120	1.409	1.426	1.211	1.000	1.106	99.36	104.22	121.58	113.53	124.89	120.0	180.0
150	1.405	1.416	1.210	1.000	1.106	99.41	105.29	120.97	113.01	126.02	150.0	180.0
180	1.403	1.412	1.210	1.000	1.106	99.44	105.88	120.62	112.81	126.57	180.0	180.0

a) The dihedral angle ϕ measures the angle of the OOH plane with respect to the COO plane and θ measures the angle of the O=CO plane with respect to the COO plane.

b) The first row represents the experimental geometry for *o*-nitroperbenzoic acid (ref 8a) and the second row is that for peroxypelargonic acid (ref 8b) (C-H bond distance is assumed).

c) Geometry was partially optimized in the syn planar conformer 3b.

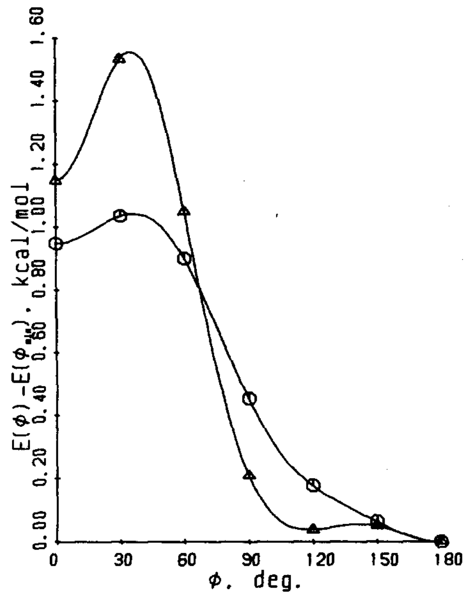


Fig. 1. Barrier to rotation about the O–O bond in peroxyformic acid. The dihedral angle, ϕ, of the OOH plane with respect to the COO plane is taken as the abscissa where $\phi = 0°$ corresponds to the *syn* planar structure of peroxyformic acid. This barrier was calculated using the STO-3G (triangles) and 5-31G basis sets (octagons). The smooth curves represent the fits of six-term Fourier expansions.

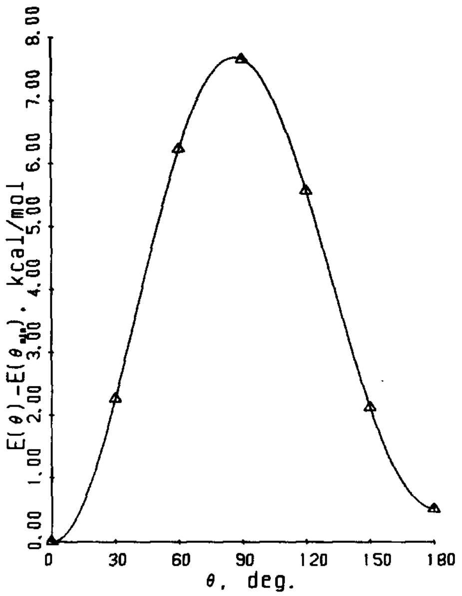


Fig. 2. Barrier to rotation about the C–O bond in peroxyformic acid (3). The dihedral angle, θ, of the O=C–O plane with respect to the COO plane is taken as the abscissa where $\theta = 0°$ corresponds to the *anti* planar structure, 3, of peroxyformic acid. The smooth curve represents the fit of a six-term Fourier expansion.

energy (kcal/mol) for the conformer whose dihedral angle is $\phi(\phi = 0°$ for the syn conformer **3b** and $\phi = 180°$ for the anti conformer **3**) relative to the energy minimum having a dihedral angle of ϕ_{min}. The parameter V_0 is the energy of the minimum energy conformer relative to the syn conformer, and the parameters V_k are the Fourier expansion coefficients which can be determined from the resulting linear system of equations. We determined the following values (kcal/mol) for the Fourier expansion coefficients representing the hindering potential for rotation about the O–O bond.

Basis Set	V_1	V_2	V_3	V_4	V_5	V_6
STO-3G	−1.575	−0.4100	0.2907	0.3681	0.1355	0.04288
5-31G	−1.118	−0.02301	0.1652	0.1067	0.005162	0.001046

It is evident from the above data that a four-term Fourier expansion would be sufficient to describe the 5-31G barrier, whereas six terms are needed with the 3G basis set. The total energies are given in Table 2. Using the above parameters, the rotational curves were generated by calculating points at 1° intervals (Fig. 1).

The STO-3G calculation of the C–O internal rotational barrier, with the minimum energy O–O rotamer taken as the ground state, was done as described above for the O–O barrier. The Fourier expansion coefficients (kcal/mol) representing this C–O rotation are:

Basis Set	V_1	V_2	V_3	V_4	V_5	V_6
STO-3G	−0.1278	7.398	0.6108	0.1192	0.0316	−0.00628

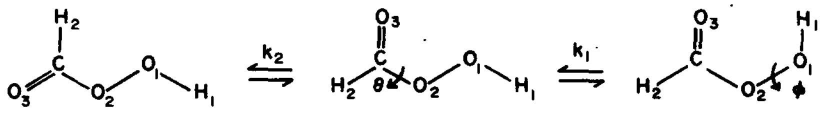
The rotational curve is presented in Fig. 2.

Finally, three conformers of H_2O_2 (bond lengths and bond angles reported by Pople)[13] and one conformer of formic acid (exhaustive optimization) were also calculated with the 3G basis set.

ROTATIONAL BARRIERS IN PEROXYFORMIC ACID

Our aim in using a MO approach to establish the preferred geometry of peroxyacids was to determine the O–O (k_1) and C–O (k_2) internal rotational barriers (eqn 1) and the significance of intramolecular H-bonding in this class of compounds.

With this dual aim in mind we initiated our studies with an investigation of the O–O barrier in the model compound, peroxyformic acid (**3**), employing INDO calculations. Using the modified X-ray geometry[8a] given in Table 1, we found that the *syn*-planar conformation **3b** is at an energy minimum that is 3.7 kcal/mol more stable that the *anti*-planar conformer **3** ($\phi = 180°$). There is a single barrier to rotation, having a maximum at $\phi = 180°$. The problems incurred by previous investigators in effectively calculating the experimental[22] *cis* (7.0 kcal/mol) and *trans* (1.1 kcal/mol) barriers to O–O



3a **3** **3b** (1)

internal rotation and the equilibrium dihedral (111° and 120°) in H_2O_2 prompted us to use an *ab initio* method of calculation.

Although rotational barriers are often calculated by maintaining a rigid geometry, it has been strongly emphasized[12,23] that the O–O barrier for H_2O_2 cannot be reliably calculated without geometry optimization at each point. The previous calculations on peroxyacetic acid employed an experimental O–O bond distance without geometry minimization. We therefore elected to optimize all geometric parameters in our study of the O–O rotational barrier in 3. The results of these total optimizations are summarized in Tables 1 and 2. Surprisingly, the O–O bond is remarkably insensitive to O–O bond rotation exhibiting only minor changes in O–O bond distance and total energy upon O–O bond rotation.[24] The shape of the rotational curve, however, was both basis set and geometry dependent with marked deviations in maxima and minima being noted without complete geometry optimization. The CO group also underwent an interesting oscillatory twist[24] as the conformer changed from *syn* to *anti*. The out of plane deviation of the CO group (θ in Table 1) was in the direction that maintained *syn*-chelated H-bonding along the early portion of the rotational curve.

Using the STO-3G basis set, we found that the minimum energy conformer for O–O rotation was the *anti*-planar structure 3. The barrier maximum occurred at $\phi \simeq 35°$ and was calculated to be 0.41 kcal/mol higher in energy than the *syn* conformer 3b. The overall *anti* to *syn* barrier is 1.55 kcal/mol. We also noted a very shallow local minimum at $\phi = 118°$ and a maximum at $\phi = 143°$ (Fig. 1).

The magnitude of these calculated (STO-3G) rotational barriers relative to the O–O barrier in H_2O_2 is surprisingly small and may well reflect in part the electronic effects of the CO group. It is also conceivable that the factors responsible for the O–O barrier (~7 kcal[22] as observed in H_2O_2) are fortuitously cancelled by the H-bonding (6–7 kcal[3c]) in the *syn* chelated conformer 3b. It is obvious that the rotational barriers are small, and for this reason we also have used extended basis sets.

Employing the 5-31G basis set we found that the shape of the O–O rotational curve was rather similar to the STO-3G curve. The major difference between the two curves is that there is less fine structure with the exten-

Table 2. Calculated total energies for peroxyformic acid conformations

Rotation-Angle (deg)		Dihedral Angles (deg)	
	E(kcal/mol)[a]	θ	ϕ
	STO-3G		
0	-163,159.70	0.0	0.0
30	-163,159.32	7.90	30.0
60	-163,159.80	7.86	60.0
90	-163,160.64	6.09	90.0
120	-163,160.81	4.03	120.0
150	-163,160.80	1.67	150.0
180	-163,160.85	0.0	180.0
0	-163,160.85	0.0	180.0
30	-163,158.59	30.0	180.0
60	-163,154.63	60.0	180.0
90	-163,153.20	90.0	180.0
120	-163,155.28	120.0	180.0
150	-163,158.73	150.0	180.0
180	-163,160.34	180.0	180.0
	5-31G		
0	-165,239.66	0.0	0.0
30	-165,239.57	7.98	30.0
60	-165,239.71	11.61	60.0
90	-165,240.16	10.73	90.0
120	-165,240.43	6.80	120.0
150	-165,240.54	2.63	150.0
180	-165,240.61	0.0	180.0

a) 1 hartree = 627.514 kcal/mol.

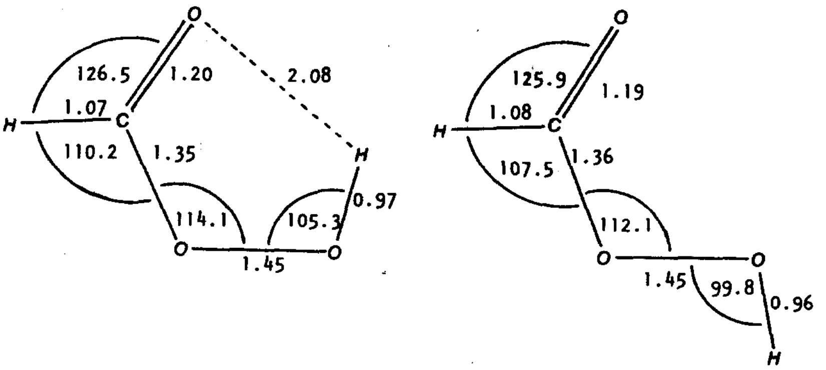
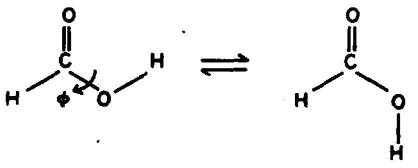


Fig. 3. Optimized geometries (5-31G) of *syn* (**3b**) and *anti* (**3**) peroxyformic acid. Bond lengths and angles are in angstroms and degrees, respectively.

ded basis set. The *anti-syn* and *syn-anti* barriers are 1.04 and 0.10 kcal/mol, respectively, with a barrier maximum at $\phi \simeq 36°$. The geometries of the *syn* and *anti* conformers are given in Fig. 3.

Significantly, the *ab initio* calculations at all levels of approximation consistently agreed that the O–O rotational barrier in **3** is ~1 kcal/mol. Thus, we may conclude that the *syn* rotational barrier for peroxyformic acid is much smaller than that calculated for H_2O_2 while it would appear that the *anti* barriers in both compounds are quite small. We also note that the calculated barrier in **3** is lower than that calculated for peroxyacetic acid (3–4 kcal/mol).



4 **4a**

Table 3. Optimized bond angles and bond distances for formic acid (**4**)

r_{H-C} 1.105A°	<HC=O	126.4°
$r_{C=O}$ 1.217A°		
r_{C-O} 1.391A°	<O=C-O	122.82°
r_{O-H} 0.993A°	<C-O-H	104.6°

Secondly, we compared the extent of H-bonding in **3b** to that in formic acid to provide a comparison to previous theoretical studies. The formic acid geometry was optimized in the *syn* conformation **4** (Table 3) since this has been reported to be 8.1[16a,16c] and 9.46[16b] kcal more stable than the *anti*-conformer **4a**. The calculated distance between the acidic hydrogen and the CO oxygen in **4** is 2.30 A° and the overlap population[28] is essentially zero, $\rho = -0.001$. This same distance is 2.08, 2.20, 2.51 and 2.90 A° in the 0°, 30°, 60° and 90° conformations of peroxyformic acid. The data in Table 4 clearly show that the O–H overlap population decreases as the angle ϕ

Table 4. Mulliken overlap population (ρ) and atomic charges (Q) for peroxyformic acid

Rotation Angle (deg)	$\rho_{C=O}$	ρ_{C-O}	ρ_{O-O}	$\rho_{O_1-H_1}$	$\rho_{O_3-H_1}$	Q_{O_3}	Q_C	Q_{O_2}	Q_{O_1}	Q_{H_1}	Q_{H_2}
					STO-3G						
0	0.8705	0.5212	0.3398	0.4766	0.0264	-0.2489	0.2542	-0.1483	-0.1731	0.2203	0.0958
30	0.8760	0.5137	0.3402	0.4786	0.0142	-0.2423	0.2512	-0.1474	-0.1656	0.2121	0.0919
60	0.8831	0.5036	0.3422	0.4794	0.0031	-0.2304	0.2489	-0.1472	-0.1585	0.2013	0.0859
90	0.8881	0.4989	0.3427	0.4807	0.0006	-0.2223	0.2514	-0.1506	-0.1593	0.1993	0.0816
120	0.8899	0.5013	0.3387	0.4834	0.0002	-0.2191	0.2553	-0.1555	-0.1627	0.2026	0.0793
150	0.8895	0.5065	0.3327	0.4853	0.0001	-0.2186	0.2580	-0.1590	-0.1644	0.2056	0.0784
180	0.8890	0.5087	0.3299	0.4857	0.0001	-0.2187	0.2588	-0.1601	-0.1647	0.2064	0.0783
					5-31G						
0	0.9217	0.1815	0.0851	0.4642	0.0427	-0.5428	0.5894	-0.3932	-0.3602	0.4642	0.2426
30	0.9368	0.1666	0.0807	0.4683	0.0315	-0.5317	0.5879	-0.3970	-0.3550	0.4567	0.2392
60	0.9649	0.1342	0.0693	0.4768	0.0126	-0.5081	0.5871	-0.4078	-0.3496	0.4465	0.2318
90	0.9862	0.1043	0.0596	0.4852	0.0029	-0.4881	0.5921	-0.4238	-0.3509	0.4453	0.2254
120	0.9982	0.0874	0.0507	0.4920	0.0004	-0.4787	0.6006	-0.4389	-0.3535	0.4490	0.2215
150	1.0037	0.0843	0.0410	0.4951	0.0000	-0.4775	0.6085	-0.4490	-0.3550	0.4524	0.2206
180	1.0052	0.0844	0.0370	0.4956	0.0000	-0.4782	0.6114	-0.4526	-0.3551	0.4537	0.2209

is increased. On the basis of these data one would not expect intramolecular H-bonding in **3b** to be significant at values of ϕ greater than 60°. The equilibrium angle of $\phi = 72°$ based upon dipole moment studies[29] is therefore probably too high if H-bonding plays a dominant role in determining the equilibrium geometry.

The C–O rotational barrier in peroxyformic acid was also calculated. The minimum conformation calculated by STO-3G ($\phi = 180°$) was chosen as the ground state. In this conformation H-bonding should not play a significant role. The one-half rotational curve resulting from rotation of the CO oxygen down toward the acidic hydrogen is given in Fig. 2. We calculated an absolute minimum ($\theta = 0°$) which was 7.68 kcal/mol below the barrier maximum ($\theta \simeq 86°$). A local minimum 0.51 kcal/mol above the ground state was found at $\theta = 180°$. By comparison, rotational barriers of 13.1 (experimental),[30] 13.2[31a] and 12.9[31b] (theoretical) kcal/mol have been reported for methyl formate.

In conclusion, the C–O internal rotational barrier in peroxyformic acid is somewhat lower than the barrier in a typical ester while a striking diminution in the O–O rotational barrier relative to that for H_2O_2 is indicated. The 5-31G calculations suggest that the molecule exhibits a minimum at its planar *anti* conformation albeit with a maximum barrier to O–O bond rotation of only ~ 1 kcal/mol. Our preferred *anti* conformer is at variance with the interpretation of experimental H-bonding studies.[3,4] The exceptionally low barrier should tax both experimental and theoretical techniques in providing an unambiguous conformational assignment. The reduction in the O–O rotational barrier is due, at least in part, to a balance between the effective H-bonding that serves to lower the energy of the molecule, and the increase in energy due to lone pair repulsion typified by the O–O barrier in hydrogen peroxide.

Acknowledgements—We wish to acknowledge partial support for this research from the National Institute of Health (ES 00761-06) and the National Science Foundation (CHE 76 21992). We also wish to thank the Wayne State University Computing Services Center for providing us with access to the Amdahl computer during the initial stages of its operation.

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[24] The O–O bond distance in peroxyformic acid is calculated to vary only 0.005 A° (3G) and 0.011 A° (5-31G) on 180° of bond rotation. Whereas the maximal carbonyl out of plane twist is 7.9° (3G) and 11.61° (5-31G) (see Table 1).

[25] We experienced considerable difficulty in getting the calculations with 4-31G basis sets to converge. This was improved when 5-31G basis set was used but about 20 iterative cycles were usually required. This situation was not improved when a different initial guess for the scaling factor which forms the off diagonal Huckel Hamiltonian elements was used.

[26] The usually small *syn* barrier for **3** prompted us to compare the barrier to internal rotation in H_2O_2 to that in **3** using the same basis set (STO-3G). Pople has reported a dihedral angle of 125° for H_2O_2[27] at the energy minimum. We found the 0° and 180° rotomers of H_2O_2 to be 10.4 and 0.2 kcal above that minimum. Hence, this method of calculation actually exaggerated the magnitude of the experimentally observed (7 kcal) *syn* barrier in H_2O_2.[22]

[27] The experimental values for H_2O_2 are $r_{OH} = 0.950$ A°, $r_{OO} = 1.475$ A°, HOO angle 94.8° and $\phi = 111.5°$ while the calculated values[13] are 1.001 A°, 1.396 A°, 101.1° and 125 ± 2°, respectively, with a total energy of − 93, 365.50 kcal/mol.

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[29] The equilibrium angle of 72° was calculated from the dipole moments of a series of aliphatic peroxyacids that averaged 2.32 D.[2] We calculate (5-31G) dipole moments of 1.662, 1.647, 1.835, 2.354, 2.958, 3.363 and 3.487 D for the 0°, 0°, 30°, 60°, 90°, 120°, 150° and 180° O–O rotamers, respectively, of per-oxyformic acid. The dipole moments calculated by the STO-3G approximation were much lower being, respectively, 1.508, 1.389, 1.419, 1.610, 1.822, 1.982 and 2.0340 for the O–O rotamers, and 2.034, 1.931, 1.739, 1.661, 1.790, 2.004 and 2.106 D

for the C–O rotamers. It should be noted that a plot of the dipole moment (μ) vs dihedral angle (ϕ or θ') reveals that μ is a minimum when ϕ or θ' correspond to a barrier maximum.

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