Effect of Bond Angle Distortion on Torsional Potentials. Ab Initio and CNDO/2 Calculations on Dimethoxymethane and Dimethyl Phosphate

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Abstract: A "coupling" of RO–X–OR (X = C or P) bond angle to rotation about the O–X bond in dimethoxymethane (DMM) and dimethyl phosphate (DMP) has been established through ab initio and semiempirical CNDO molecular orbital calculations. Analysis of structural data (x ray and electron diffraction) on related molecules supports this conclusion. Specifically, rotation about the O–X bond from a gauche to a trans conformation results in ca. a 5° reduction in the O–X–O bond angle. Thus, the CNDO optimized O–C–O bond angle in DMM is 112° for the g,g conformation, 107° for the g,t conformation, and 102° for the t,t conformation (ab initio geometries are comparable). A similar change is observed for DMP. This bond angle distortion may be useful in identifying important interactions between lone electron pairs and bonds, which are suggested to be responsible for the observed bond angle variation. Reversal of the relative energies for the g,g and g,t conformations is possible without bond angle optimization in the calculations and establishes the importance of optimization of this geometric parameter in molecular orbital torsional barrier calculations.

The necessity for complete geometry optimization in the accurate prediction of molecular structure and energies by ab initio and semiempirical molecular orbital methods has long been recognized. Predictions of correct torsional angles and barriers to internal rotation can be especially sensitive to the proper initial choice of geometry or require full geometry optimization. Thus, the torsional potential for hydrogen peroxide was not correctly predicted by even the extended basis set ab initio calculations[2,3] until complete geometry optimization including the bond angle, bond distances, and torsional angle was considered.[4,5] In other molecules such as ethane, geometry optimization is relatively unimportant.[5]

We have recently demonstrated that geometry optimization is important in accurately gauging equilibrium torsional geometries and barriers in dimethyl phosphate monoanion and trimethyl phosphate.[6,12b] Through semiempirical CNDO/2 molecular orbital calculations we demonstrated a coupling of ester O–P–O bond angles and torsional angles in these phosphate esters. In this paper we wish to demonstrate an analogous coupling of O–C–O bond angles and torsional angles in dimethoxymethane, $(CH_3O)_2CH_2$ (DMM), using both CNDO and ab initio calculations and x-ray crystallographic data.

Method of Calculation

Dimethoxymethane was modeled on the basis of x-ray crystallographic structural data on the anomeric carbon of sugars (see references in Table I). The dimethyl phosphate structure has been described previously.[6] The semiempirical SCF-LCAO-MO calculations employed the CNDO option in the CNINDO/2 program of Pople and Segal.[7a] The ab initio calculations used the GAUSSIAN 70 system of programs with a STO-3G basis set.[7b] In the CNDO calculations, only the valence basis orbitals were considered, and for phosphorus, 3d orbitals were included. The major structural parameters that we have varied in the dimethoxymethane and dimethyl phosphate models are the O–C–O and O–P–O bond angles, θ, and the two dihedral angles ω and ω' defined in Figures 1 and 2. The angle θ' in these figures is determined by the assumed C_{2v} symmetry of the central carbon and phosphate tetrahedra, the fixed O–P–O or H–C–H bond angles, and the variable bond angle, θ. Dihedral angles are defined by clockwise rotation about the RO–X–OR (see ref 8 for convention).

Results and Discussion

As demonstrated in Figures 3 and 4 for DMM and DMP either the gauche, gauche (g,g) or gauche, trans (g,t) conformations may represent the minimum energy conformation, *depending upon the choice of the O–X–O (X = C or P) bond angle.* Thus, as shown in Table I and Figure 3 for DMM, the g,g conformation is 1.2 kcal/mol more stable than the g,t conformation when an O–C–O bond angle of 112° is assumed. However, if the O–C–O bond angle is constrained to 107°, then the g,t conformation is now preferred by ca. 0.5 kcal/mol over the g,g conformation. (The same reordering of energies is also observed in the STO-3G ab initio calculations, Table I.) As discussed in ref 6 and illustrated in Figure 4, a similar "coupling" of torsional angles to bond angles was established for DMP. Obviously, in calculating torsional potentials and predicting optimized torsional angles for molecules such as DMM or DMP the choice of bond angles becomes critical.

The two-dimensional, energy vs. torsional angle plot of Figure 3 was extended by computing a bond angle–torsional angle energy surface. We have computed the energy of DMM with one gauche (ω = 60°) and a second variable torsional angle and a variable O–C–O bond angle (θ). The torsional angle was varied between 30 and 240° at 30° intervals and the bond angle was varied between 105 and 115° in 2–3° increments. The contour map created from these calculations is shown in Figure 5. A similar contour map for DMP was presented in ref 6. Because more extensive calculations were performed with the CNDO method, unless otherwise specified, further discussion will refer to the CNDO calculations.

As suggested by the earlier calculations (Figure 3), the g,g conformation is still shown to be the lowest energy structure (Figure 6) and the optimized O–C–O bond angle for this conformation is 112° (114.7°, ab initio result).

The acetal in a g,t conformation minimizes its energy by distorting the O–C–O bond to 107° (109.4°, ab initio result). As shown in Figure 6 DMM in a t,t conformation is predictd to prefer an O–C–O bond angle of 102° (103.8°, ab initio result).

These calculations indicate that rotation about the C–O bond (and P–O bond in DMP) produces significant bond angle distortion. The optimized O–C–O bond angle and the minimum energy for DMM as a function of the second torsional angle in this "flexible rotor" are plotted in Figure 7. By optimizing the bond angle, the g,t conformation is now only 0.4 kcal/mol (1.57 kcal/mol, ab initio) higher energy than the optimized g,g structure. Dimethyl phosphate shows exactly analogous bond angle distortions. Each rotation from a gauche

Table I. Comparison of ab Initio and CNDO Calculations on Dimethoxymethane

Torsional conformation	Method	Unoptimized geometry θ, deg	Unoptimized geometry E,[a] kcal/mol	Optimized geometry θ, deg	Optimized geometry E,[a] kcal/mol
g,g	CNDO	112	0.00	111.7	0.00
g,g	ab initio	108	0.25	114.66[c]	0.00[b]
g,t	CNDO	112	1.18	107.5	0.43
g,t	ab initio	108	0.00	109.35[d]	1.57
t,t	CNDO	112	3.37	103.3	0.78
t,t	ab initio	108	2.58	103.72[e]	3.33

[a] Relative energy for geometry shown in Figure 1 unless otherwise specified. [b] Total energy −264.5483 au. [c] Optimized H-C-H bond angle, 108.36°. [d] Optimized H-C-H bond angle, 107.54°. [e] Optimized H-C-H bond angle, 106.90°.

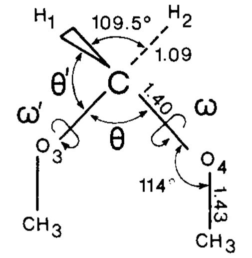


Figure 1. Structure of dimethoxymethane. $\omega = \omega' = 0°$ represents the cis, eclipsed conformation, as drawn. $\angle O_3CH_1 = \angle O_3CH_2 = \angle O_4CH_1 = \angle O_4CH_2 = \theta'$.

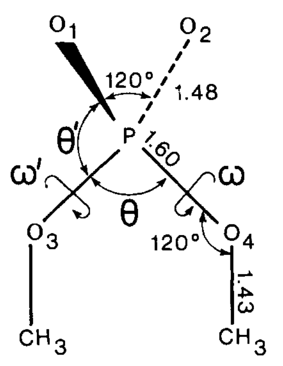


Figure 2. Structure of dimethyl phosphate monoanion, drawn in the cis, eclipsed conformation. $\angle O_1PO_3 = \angle O_1PO_4 = \angle O_2PO_4 = \angle O_2PO_3 = \theta'$.

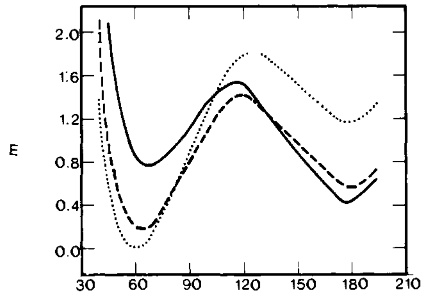


Figure 3. Plot of relative energy vs. the torsional angle, ω, for O-C-O bond angles (θ) 112° (···), 107° (—), and 109.4° (- - -) in DMM. Other torsional angle, ω′, was kept constant at +60°.

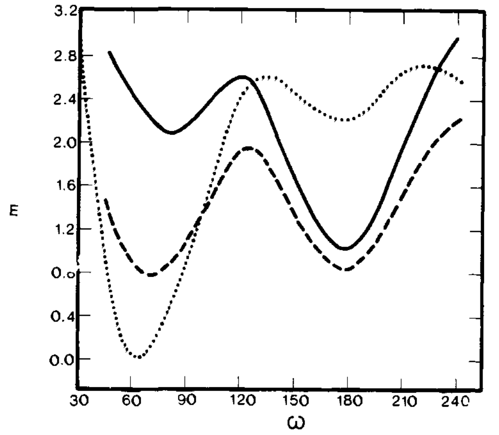


Figure 4. Plot of relative energy vs. the torsional angle ω for RO-P-OR bond angles (θ) 104° (···), 98° (- - -), and 95° (—) in DMP. Other torsional angle, ω′, was kept constant at +64°.

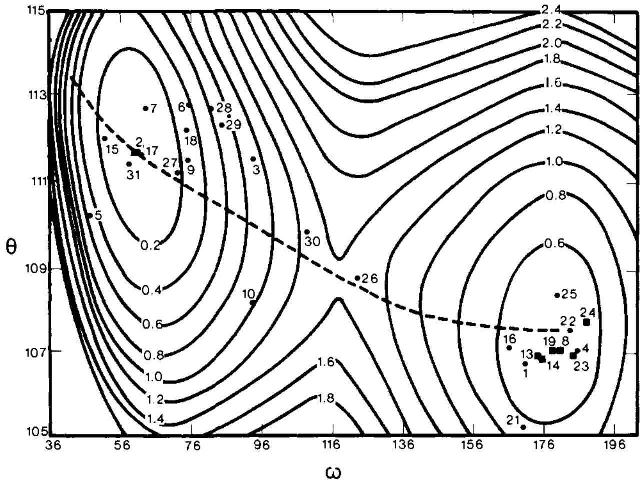


Figure 5. Bond angle (θ)-torsional angle (ω) energy contour map of DMM. The other dihedral angle was fixed at +60°. Isoenergy contours are in kcal/mol over the lowest energy geometry ($\omega = \omega' \sim 60°$, $\theta \sim 112°$). Points (●, ■) and numbers refer to acetal geometries in Table I. Other dihedral angle not plotted is ca. +g (●) or anticlinal (■). Dotted line represents the optimized bond angle for a given conformation.

to a trans conformation results in ca. a 5° reduction in the O-X-O bond angle.

Although CNDO calculations may give very good torsional barriers as supported by ab initio calculations, they may often as not be quite inaccurate. It is quite satisfying that at least in these molecules the two methods yield surprisingly similar results. Furthermore, additional support for this calculated coupling effect is provided in an analysis of the x-ray and electron diffraction structures of compounds with the O-C-O structural fragment. Thus, included in Figure 5 are the bond and torsional angles of various sugars and related structures listed in Table II (only the torsional angle differing most from the +g conformation is plotted and any compound with a −g conformation is converted to the conformation of its mirror image for the purpose of plotting Figure 5). Although some scatter is found, the correlation is found to be quite good. For the 13 structures possessing the g,g (or −g,−g) conformations, the average O-C-O angle is 111.83 ± 0.73°, while for the 13 structures possessing the g,t (or −g,t) conformation the average O-C-O angle is 107.11 ± 0.78°. The data quite clearly sepa-

Table II. X-Ray and Electron Diffraction Structural Data on Molecules Containing the O–C–O Structural Unit

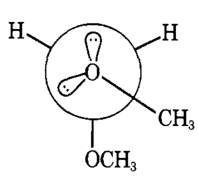
Compd	RO–C–OR bond angle θ, deg	Dihedral angles ω, ω′, deg
X-Ray Diffraction Data		
Monosaccharides		
1. 4,6-Dideoxy-4-(*N,N*-dimethylamino)-α-D-talopyranoside methiodide[a]	106.7	170.7, 75.0
2. Methyl α-D-mannopyranoside[b]	111.7	59.8, 60.9
3. α-D-Xylopyranose[c]	111.5	−62.1, −93.6
4. Methyl β-xyloside[d]	107.0	174.5, −72.3
5. α-L-Sorbose[e]	110.2	−60.0, −47.4
6. β-DL-Arabinose[f]	112.8	60.7, 75.3
7. Methyl α-D-glucopyranoside[g]	112.7	59.3, 63.0
8. β-D-Glucose[h]	107.0	−179.4, −95.0
9. α-D-Glucose[i]	111.5	60.0, 74.9
10. α-D-Glucopyranose urea[j]	108.1	59.9, 93.3
11. Plant sulfolipid-A glucose derivative[k]	108.6	63.7, 65.4
12. α-L-Rhamnopyranose monohydrate[l]	111.9	−65.2, 95.8
13. 2-Amino-2-deoxy-β-D-galactopyranose hydrochloride (molecule A)[m]	106.9	174.3, 98.3
14. "Same" (molecule B)[m]	106.8	175.3, 93.7
15. Methyl α-D-altropyranoside[n]	112.0	51.6, 63.8
16. Methyl 3,6-anhydro-α-D-galactopyranoside[o]	107.1	166.1, 68.1
Disaccharides		
17. α,α-Trehalose dihydrate[p]	111.6	58.6, 61.7
18. α,α-Trehalose dihydrate[p]	112.2	56.6, 74.6
19. α-Lactose monohydrate[q]	107.0	−178.3, −94.2
20. α-Lactose monohydrate[q]	111.5	146.1, 59.0
21. 3,6-Anhydro-α-D-glucopyranosyl-1,4:3,6-dianhydro-β-D-fructofuranoside[r]	105.2	170.1, 84.0
22. Cellobiose[h]	107.5	176.7, −76.3
23. Cellobiose[h]	106.9	175.6, −116.3
24. Methyl β-cellobioside methanol[t]	107.7	−172.0, 91.1
25. Methyl β-cellobioside-methanol[t]	108.3	−179.8, −76.2
26. β-Maltose monohydrate[u]	108.7	59.5, 123.1
Trisaccharides		
27. Raffinose pentahydrate[v]	111.2	60.4, 71.9
28. Raffinose pentahydrate[v]	112.7	59.7, 81.7
29. 1-Kestose[w]	112.3	60.2, 84.6
30. Planteose dihydrate[x]	109.8	60.1, 108.6
31. Planteose dihydrate[x]	111.4	60.2, 58.5
Electron Diffraction Data		
Acyclic		
32. Dimethoxymethane[y]	112.6	66.3, 66.3
33. Tetramethoxymethane[z]	114.6	63.1, 63.1
	106.9	63.1, t

[a] R. E. Cook and M. D. Glick, *Acta Crystallogr., Sect. B,* **26,** 1741 (1970). [b] B. M. Gatehouse and B. J. Poppleton, *ibid.,* **26,** 1761 (1970). [c] A. Hordvik, *Acta Chem. Scand.,* **25,** 2175 (1971). [d] C. J. Brown and (in part) Sir G. Cox and F. J. Llewellyn, *J. Chem. Soc. A,* 922 (1966). [e] S. H. Kim and R. D. Rosenstein, *Acta Crystallogr.,* **22,** 648 (1967). [f] S. H. Kim and G. A. Jeffrey, *ibid.,* **22,** 537 (1967). [g] H. M. Berman and S. H. Kim, *Acta Crystallogr., Sect. B,* **24,** 897 (1968). [h] S. C. C. Shirley and G. A. Jeffrey, *Acta Crystallogr., Sect. B,* **24,** 830 (1968). [i] G. M. Brown and H. A. Levy, *Science,* **147,** 1038 (1965). [j] R. L. Snyder and R. D. Rosenstein, *Acta Crystallogr., Sect. B,* **27,** 1969 (1971). [k] Y. Okaya, *Acta Crystallogr.,* **17,** 1276 (1964). [l] R. C. G. Killean, J. L. Lawrence, and V. C. Sharma, *Acta Crystallogr., Sect. B,* **27,** 1707 (1971). [m] M. Takai, S. Watnabe, T. Ashida, and M. Kakudo, *ibid.,* **28,** 2370 (1972). [n] B. M. Gatehouse and B. J. Poppleton, *ibid.,* **27,** 871 (1971). [o] J. W. Campbell and M. M. Harding, *J. Chem. Soc., Perkin Trans. 2,* 1721 (1972). [p] G. M. Brown, D. C. Rohrer, B. Berking, C. A. Beevers, R. O. Gould, and R. Simpson, *Acta Crystallogr., Sect. B,* **28,** 3145 (1972). [q] D. C. Fries, S. T. Rao, and M. Sundaralingam, *ibid.,* **27,** 994 (1971). N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc., Perkin Trans. 2,* 582 (1972). [t] J. T. Ham and D. G. Williams, *Acta Crystallogr., Sect. B,* **26,** 1373 (1970). [u] G. J. Quigley, A. Sarko, and R. H. Marchessault, *J. Am. Chem. Soc.,* **92,** 5834 (1970). [v] H. M. Berman, *Acta Crystallogr., Sect. B,* **26,** 290 (1970). [w] G. A. Jeffrey and Y. J. Park, *ibid.,* **28,** 257 (1972). [x] D. C. Rohrer, *ibid.,* **28,** 425 (1972). [y] E. E. Astrup, *Acta Chem. Scand.,* **25,** 1494 (1971). [z] F. C. Mijlhoff, H. J. Geise, and E. J. M. van Schaick, *J. Mol. Struct.,* **20,** 393 (1973).

rate into two well-defined groups, as is verified by analyzing the separability of the sets by the F-statistical test. The few structures that cannot be classified g,g or g,t even exhibit the optimized O–C–O bond angle predicted for that conformation (dotted line in Figure 5). Sundaralingam has also qualitatively noted a conformational dependence to the O–C–O bond angles at the anomeric carbon of sugars.[8b] X-ray crystallographic data for phosphate diester monoanions and neutral triesters similarly confirm the dependence of bond angle on torsional angle.[6]

Gauche Effect. There have been a number of other semiempirical and ab initio MO calculations on the torsional potential in molecules with the RO–C–OR and RO–P–OR structural fragments.[6,9–15] All calculations have confirmed the experimental observation that the g,g conformation is the lowest energy structure. The preference for this conformation in molecules of this type has been variously described as the "generalized anomeric", "Edward-Lemieux", or "gauche" effect.[16–19] The lower energy for an axial hydroxyl group over an equatorial hydroxyl at the anomeric carbon of pyranoses (the anomeric effect) has been ascribed to this conformational preference.[18] Various quantum mechanical studies involving decomposition of the torsional potentials into Fourier components[9,17] and energy components[16] have been offered to explain these results.

Origin of Bond Angle Coupling to Torsional Angles. A very simple explanation for the observed 5–6° reduction in O–X–O bond angle for each rotation about the O–X bond from a gauche to a trans conformation (i.e., g,g → g,t → t,t) is made clear in the Newman projections, structures I and II. Although the following argument will apply to both DMM and DMP, and indeed any molecule with structure -O-X-O-, where X is a tetracovalent atom, we limit our discussion to DMM. There are two CH_3-O-C-H gauche bond-bond interactions in the trans structure, II (interacting bonds are indicated by heavier lines), whereas there is one H_3C-O-C-H gauche interaction and one CH_3-O-C-O gauche interaction in the gauche structure, I. For the trans conformation, the geometrical distortion which will minimize these bond-bond gauche repulsions[20] is a decrease in the O–C–O bond angle, θ (with a concomitant increase in the O–C–H bond angle, θ′). Note that this



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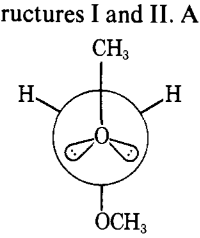

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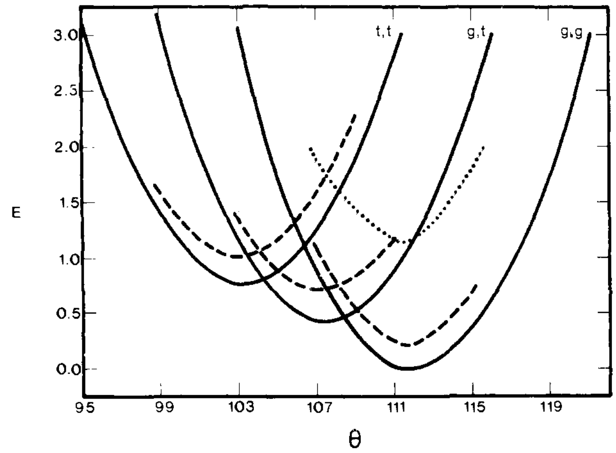
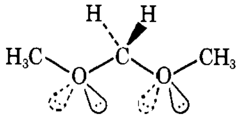


Figure 6. Relative energy vs. O-C-O bond angle, θ, for DMM in g,g (—), g,t (—), and t,t (—) conformations. Dashed lines (- - -) represent identical plots except the H-C-H bond angle has been reduced to 112°. Dotted line (···) represents plot for DMM in g,g conformation with H-C-H bond angle of 116°.

bond angle distortion which minimizes the bond-bond repulsion *increases* the repulsion between the C-O bond and the two oxygen nonbonding pairs.

It appears therefore that bond-bond repulsion is greater than bond-lone pair repulsion. This conclusion conflicts with the Gillespie-Nyholm electron-pair repulsion theory[21] which holds that lone pair-lone pair repulsions are greater than lone pair-bond repulsion which in turn is greater than bond-bond repulsion. Our conclusion however does support the claim of Wolfe et al.[16b] that the nonbonded pairs in molecules such as DMM create quasispherical potential fields and that the directed ligand picture of a lone pair as suggested by structures I and II is not a very accurate one.

The apparent "invisibility" of these directed lone pairs is perhaps best demonstrated in the bond angle distortion found for the trans, trans conformation, III. Several explanations for the anomeric effect have emphasized the importance of lone pair-lone pair repulsions,[8,22,23] i.e., the "rabbit ear" effect.[24] Note that in structure III there are two sets of eclipsed lone pairs which according to the "rabbit ear" argument should disfavor the t,t conformation relative to the g,g and g,t conformations. However, the *optimized O-C-O bond angle, θ, in III is even smaller* (θ_{min} = 102°) *than that in the g,g or g,t conformations*, counter to the direction expected for repulsive lone pair-lone pair interactions.[21,25] These distortional effects thus firmly support the interpretation that lone pair-lone pair effects are not responsible for the gauche (or anomeric) effect. Rather, bond-bond interactions must largely determine stereochemistry.[16]



III

These simple bond-bond interaction arguments also explain other distortions from tetrahedral symmetry in these molecules. Thus, in g,g DMM the optimized O-C-O bond angle is 112° whereas in the g,g DMP the optimized bond angle is 105°. As shown in Newman projection IV for g,g DMM, enlarging the O-C-O bond angle by 3° from the normal tetrahedral value reduces the H_3C-O-C-O bond-bond repulsion at the expense of increasing the H_3C-O-C-H bond-bond repulsion. In V, the 4° reduction from tetrahedral in the O-P-O bond angle of DMP increases the H_3C-O-P^+-OR bond-bond repulsion but decreases the H_3C-O-P^+-O^- repulsion. One may conclude (as our chemical intuition guides us) that the more polar the bond (i.e., P^+-O^-), the greater the polar bond-polar bond repulsion. Wolfe et al.,[16b] however, argue that polar bond interactions are smaller than nonpolar bond interactions. Analysis of bond angle distortions should be an important tool in discovery of the stereochemical consequence of electron pair and bond interactions.

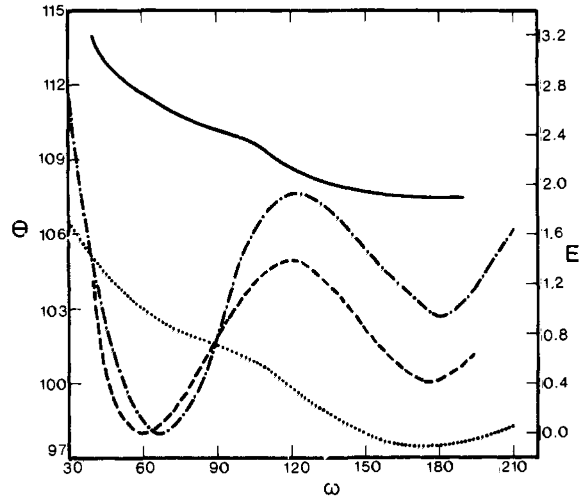
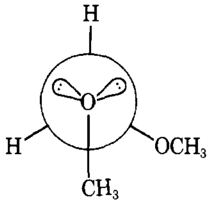


Figure 7. Plot of optimized bond angle for DMM (—) and DMP (···) vs. torsional angle, ω (left-hand scale). Plot of relative energy for DMM (- - -) and DMP (- · -) with optimized bond angle vs. ω (right-hand scale). The other torsional angle was kept constant at +gauche.



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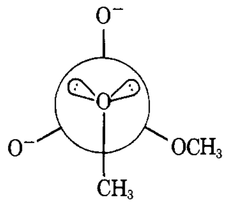
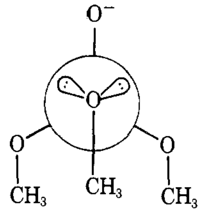


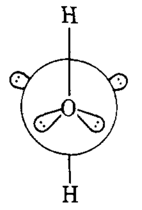
V

Finally, the optimized RO-P-OR bond angle in trimethyl phosphate in the g,g conformation is calculated (and experimentally confirmed) to be ca. 108°.[6] This nearly tetrahedral bond angle is expected for a symmetrical arrangement of groups as shown in structure VI. Again, these conclusions have been reached by *ignoring the nonbonded electron pairs.*[26]



VI

Bond Angle Optimization in Related Structures. We have already noted that the correct geometry and torsional potentials for hydrogen peroxide were predicted only when geometry optimization was included in the MO calculations.[4] The same principles used to explain bond angle distortions in DMM and DMP may be shown to apply to hydrogen peroxide and other molecules as well. The optimized O-O-H bond angle for the trans conformation, VII, of H_2O_2 is calculated by Veillard[4] to be 100.2°, whereas for the gauche conformation, VIII, the optimized bond angle is 103.9°. The 3.7° larger bond angle for the gauche conformation is consistent with our chemical intuition that this larger angle minimizes the gauche, H-O-O-H



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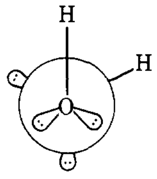

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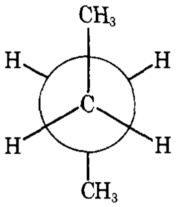

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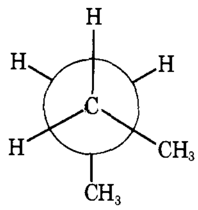

X

bond-bond repulsion. A similar distortional effect is observed in *n*-butane,[27] where for the trans conformation, IX, the C-C-C bond angle is calculated to be 112.3° while the C-C-C bond angle in the gauche conformation X, is 113.4°. Although the magnitude of the bond angle distortion is much smaller (1.1°), we see again that the larger angle is found in the gauche conformation. The small bond angle distortion in *n*-butane and the much larger bond angle distortion in DMM, DMP, and H_2O_2 further establish that these effects are due largely to bond-bond interactions rather than bond-lone pair or lone pair-lone pair interactions. Thus, it appears that the largest bond angle distortional effects will be found in molecules such as DMM or DMP where two gauche bond-bond interactions oppose two gauche bond-lone pair interactions. Apparently the bond-lone pair interactions are less important and the "invisible" lone pairs therefore do not appear to influence these bond angle distortions.

Significance of Geometry Optimization in Torsional Barrier Calculations. Several approaches have been taken in the calculation of barriers to internal rotation:

(1) The rigid rotor approximation. Rotation about a bond keeping the bond lengths and bond angles fixed. Either (a) experimentally determined bond langths and angles or (b) standard bond angles and bond lengths are assumed.

(2) The partially flexible rotor. Generally involves either (a) optimization of the "most important" geometric parameters at each conformation or (b) geometry optimization at the minimum energy conformations.

(3) The flexible rotor. Full geometry optimization at each torsional conformation.

experimentally determined bond lengths and angles or (b) standard bond angles and bond lengths are assumed.

In many instances theoretical torsional potentials are calculated using the least sophisticated rigid rotor approximation, 1. However, in some molecules such as hydrogen peroxide, DMM, and DMP, the fully flexible rotor calculation is strongly indicated. The fully flexible rotor calculation is not often performed because of the tremendous computing expense involved in finding global energy minima on structural hypersurfaces.[28] Our results have shown that great care must be exercised in using the rigid rotor approximation as a viable alternative to the complete geometry optimization procedures. Specifically as shown in Figures 3 and 4, an inappropriate choice of bond angles in DMM and DMP can yield results directly opposite to experiment and optimized geometry, MO calculations. In addition, optimization of the structure may produce significant energy reductions for only certain conformations. The use of a fixed O-C-O bond angle of 112° for DMM gives an energy for the t,t conformation which is ca. 3.0 kcal/mol higher than the bond angle optimized energy. Relaxing the O-C-O bond angle in the g,t conformation dramatically decreases the energy difference between the g,t and g,g conformations (1.2 to 0.4 kcal/mol). Note also that approximation 1b (fixed standard geometries) is preferable to approximation 1a (experimental geometries assumed), since the experimental bond angles will reflect the experimental torsional conformation of the molecule. To avoid prejudicing the torsional potential calculation by using experimental bond angles, it is better to simply assume fixed, standard tetrahedral (or trigonal, etc.) bond angles. As shown in Figure 3 when a tetrahedral O-C-O bond angle is assumed in DMM, the g,g conformation is more stable than the g,t conformation. The energies for the two conformations and the barrier height are altered, but at least the relative ordering of the two conformations is correct. Unfortunately, some recent semiempirical and ab initio MO torsional potential calculations on DMM[10] and DMP[11,12,14] have used experimental, nontetrahedral bond angles. Since geometry optimization was not performed, these results should be carefully considered.

We have only considered the effect of a single bond angle adjustment (although both θ and θ' change) on the torsional energy surfaces. However, this O-X-O bond angle, θ, variation is likely the single most important geometric distortion influencing the relative energies of the different conformations and torsional barriers. Thus, as shown in Figure 6 alteration of the fixed H-C-H bond angle in DMM raises the energies of the g,g, g,t, and t,t conformations by nearly the same amount. The energy differences between the conformations and optimized O-C-O bond angles are nearly invariant to changes in the H-C-H bond angle. In addition ab initio geometry optimization on the H-C-H and O-C-O bond angles shows only small variation of the H-C-H bond angle with torsional conformation (Table I). Perahia et al.[12] have also noted that variation of θ' alone influences the relative energies of the DMP conformations. However, their energy changes are much smaller than those achieved by optimizing θ. Jeffrey et al.[9a] have demonstrated in ab initio calculations on dihydroxymethane that the C-O bond lengths are "coupled" to the torsional conformation. However, the energy of the dihydroxymethane changes by only $\sim$0.2 kcal/mol in using optimized bond lengths rather than standard bond lengths for all conformations. As we have shown, optimization of the O-X-O bond angle (resulting in a change as large as 12°) can alter the energy of DMM and DMP by over 5.0 kcal/mol. Since this bond angle distortion is likely po be generally important in tetrahedral molecules where lone pair-bond interactions are possible,[30] serious consideration should be given to at least optimize an appropriate bond angle in any torsional barrier calculation if full geometry optimization is impossible.

Finally we have recently demonstrated[31] that the conformational dependence to heavy atom chemical shifts and directly bonded coupling constants is likely attributed to the bond angle deformation resulting from torsional bond angle changes.

Note Added in Proof. Further CNDO and ab initio calculations on DMP demonstrate that geometry optimization can dramatically alter the relative energies of the conformational isomers of the phosphate ester (D. G. Gorenstein, B. A. Luxon, and J. B. Findlay, *Biochim. Biophys. Acta*, in press). Thus, with ab initio geometry optimization (again, particularly the RO-P-OR bond angle) the energy difference between the g,g, g,t, and t,t conformations is *less than 1 kcal/mol* rather than ca. 7 kcal/mol previously reported.[11]

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(26) The bond angle distortions in IV–VI may also be rationalized in terms of competing lone pair–bond vs. bond–bond interactions. Thus, decreasing the O–P–O bond angle in V would reduce the repulsion between the nonbonded pair and two $P^+–O^-$ bonds. In IV, the larger O–C–O bond angle could reflect the less unfavorable gauche interaction of a lone pair with two nonpolar C–H bonds.

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(29) The CNDO calculations are not able to reproduce the specific bond length coupling to torsional geometry calculated in ref 12 (D. G. Gorenstein and D. Kar, unpublished results).

(30) Significantly, the bond angle distortion is quite similar for both DMP and DMM, as shown in Figure 7, and is *not the result of steric hindrance* (distances between any of the atoms are well beyond the sum of the van der Waals radii).

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Ab Initio Theoretical Studies of the Rydberg States of Formaldehyde[1]

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Abstract: Ab initio configuration interaction (GVB–CI) methods are used to study the excited Rydberg states of formaldehyde formed by exciting out of either the n or π orbital into the various 3s, 3p, and 3d-like Rydberg orbitals. The resulting excitation energies are in good agreement (within ~0.1 eV) with the available experimental results. Calculated oscillator strengths are in fair agreement with experiment. Two states $^1(\pi \rightarrow \pi^*)$ and $^1(\pi \rightarrow 3s)$ are calculated to lie between 10.7 and 10.8 eV, corresponding closely to a broad unassigned peak in the electron impact spectrum (10.5–11.0 eV). We have assigned other peaks in the electron impact spectrum at 11.4–12.0 eV and 12.5–12.8 eV as resulting from $(\pi \rightarrow 3p)$ and $(\pi \rightarrow 3d)$ transitions, respectively.

I. Introduction

The electronic states of simple organic molecules can be categorized according to size as either valence or Rydberg. In a previous paper[2] we reported the results of ab initio generalized valence bond (GVB) calculations on the valence states of formaldehyde, $^{3,1}(n \rightarrow \pi^*)$ and $^3(\pi \rightarrow \pi^*)$. It is the purpose of this paper to extend this treatment to the Rydberg states.

The Rydberg states of formaldehyde have been the subject of numerous recent experimental[3-9] and theoretical[9-15] investigations. Experimentally, dipole-allowed n → s, n → p, and n → d Rydberg series have been assigned in both the optical and electron impact spectra. However, there has been no conclusive assignment of a Rydberg state resulting from excitation out of the π orbital (we denote such states as π Rydberg) in either the optical or electron impact spectra. In