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Charge-Density Analysis of Rotational Barriers¹

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Abstract: Electron-density-distribution plots determined from accurate *ab initio* LCAO-MO-SCF wave functions are used to elucidate the mechanism of rotational barriers. Barriers in ethane and acetaldehyde are examined. Charge-density analysis enhances physical understanding of rotational barriers, and it is shown to be consistent with their repulsive or attractive dominant nature. The origin of rotational barriers is seen to arise from ordinary chemical bonding on a small scale.

Electron-density-distribution analysis has proved to be an effective means of interpreting various aspects of chemical bonding,² molecular orbital wave functions,² and molecular geometry.³ In this work, electron-density distributions obtained from LC-(Hartree-Fock)AO-MO-SCF wave functions have been used to analyze barriers to internal rotation in ethane and acetaldehyde. These two molecules were chosen for two important reasons: threefold barriers have been by far the most widely studied; secondly, all barriers can be classified as being repulsive or attractive dominant,⁴ and ethane is representative of the former and acetaldehyde of the latter class. The present analysis was carried out to obtain a better physical understanding of the origin of rotational barriers and to characterize the associated electron density distortions in terms of the barriers' repulsive and attractive dominant natures.

(1) Research supported by Chemistry Programs, National Science Foundation, Grant No. GP 8907.

(2) B. J. Ransil and J. J. Sinai, *J. Chem. Phys.*, **46**, 4050 (1967), present an extensive review of articles on charge-density analysis; see also R. F. W. Bader, W. H. Henneker, and P. E. Cade, *ibid.*, **46**, 3341 (1967); R. F. W. Bader, I. Keavenly, and P. E. Cade, *ibid.*, **47**, 3381 (1967); P. A. Kollman, J. F. Liebman, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1142 (1970); P. A. Kollman and L. C. Allen, submitted for publication.

(3) (a) C. W. Kern and M. Karplus, *J. Chem. Phys.*, **40**, 1374 (1964). (b) R. J. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *ibid.*, **45**, 2835 (1966).

(4) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968). Barrier mechanisms are analyzed using the energy components $V_{att} \equiv V_{ne}$ and $V_{rep} \equiv V_{ee} + V_{nn} + T$.

Computational Procedures and Formulation

For the ethane barrier, the wave functions for the eclipsed and staggered configurations were taken from earlier work in this laboratory.⁵ The two geometries are illustrated in Figure 1 and the corresponding coordinates of the atomic centers are listed in Table I.

Table I. Coordinates of Atoms^a

	X	Y	Z
Staggered Ethane			
C ₁	0.0	0.0	0.0
C ₂	0.0	0.0	2.9159
H ₁	1.69855763	-0.98066292	-0.69996172
H ₂	-1.69855763	-0.98066292	-0.69996172
H ₃	0.0	1.96132584	-0.69996172
H ₄	1.69855763	0.98066292	3.61586171
H ₅	0.0	-1.96132584	3.61586171
H ₆	-1.69855763	0.98066292	3.61586171
Eclipsed Ethane ^b			
H ₄	1.69855763	-0.98066292	3.61586171
H ₅	-1.69855763	-0.98066292	3.61586171
H ₆	0.0	1.96132584	3.61586171

^a In atomic units. Data from ref 5. ^b C₁, C₂, H₁, H₂, and H₃ remain the same as above.

The overlap populations and gross atomic charges for the wave functions are presented in Table II. The staggered conformer was calculated to be 2.521 kcal/

(5) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

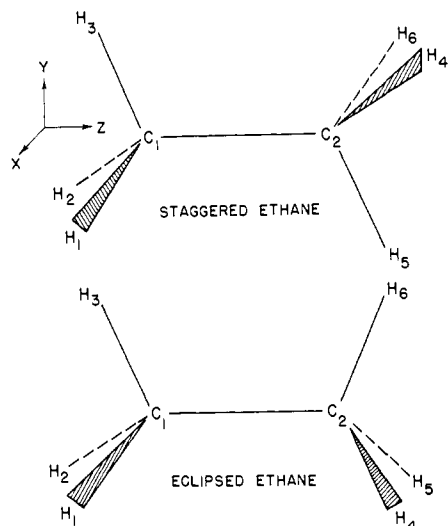


Figure 1. Configurations for ethane.

mol more stable than the eclipsed, in reasonable agreement with the experimental barrier magnitude of 2.928 ± 0.025 kcal/mol.⁶

Table II. Mulliken Overlap Populations for Ethane

Atom 1	Atom 2	ρ_{12} (staggered)	ρ_{12} (eclipsed)
C ₁	C ₂	0.49281	0.48096
C ₁	H ₁	0.76877	0.76998
C ₁	H ₄	-0.04931	-0.04940
H ₁	H ₄	-0.00174	-0.00587
H ₁	H ₆	0.00105	0.00085
H ₁	H ₂	-0.01364	-0.01355
Atomic charges from population analysis for ethane			
Atom	Staggered	Eclipsed	
C	6.81657	6.81719	
H	0.72784	0.72761	

Wave functions also determined in this laboratory were used for the two extreme conformations of acetaldehyde.⁷ The configuration with a methyl hydrogen eclipsing the C-O double bond was found to be 1.09 kcal/mol more stable than the form with a methyl hydrogen eclipsing the aldehyde hydrogen. This is in good agreement with the experimental value of 1.16

Table III. Coordinates of Atoms^a

	X	Y	Z
H-Eclipsing-O Acetaldehyde			
C ₁	0.0	-2.837	0.0
C ₂	0.0	0.0	0.0
O	0.0	1.282	1.907
H ₁	0.0	-3.563	1.91934952
H ₂	1.66220545	-3.563	-0.95967476
H ₃	-1.66220545	-3.563	-0.95967476
H ₄	0.0	0.972	-1.867
H-Eclipsing-H Acetaldehyde ^b			
H ₁	1.66220545	-3.563	0.95967476
H ₂	0.0	-3.563	-1.91934952
H ₃	-1.66220545	-3.563	0.95967476

^a In atomic units. ^b C₁, C₂, O, and H₄ remain the same as above.

(6) S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

(7) R. B. Davidson and L. C. Allen, *ibid.*, in press.

ACETALDEHYDE

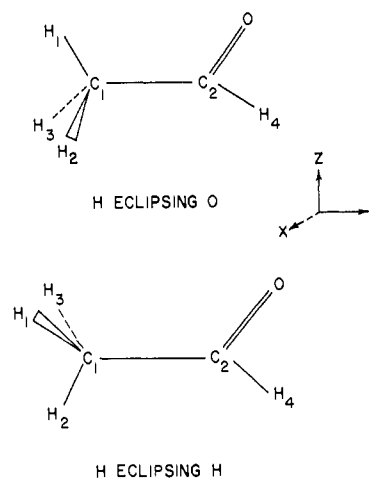


Figure 2. Configurations for acetaldehyde.

kcal/mol.⁸ In the following, these two geometries are called the H-eclipsing-O and H-eclipsing-H conformers, respectively. Both are illustrated in Figure 2, and the coordinates of their substituent atoms listed in Table III. The overlap populations and atomic charges for both conformations are presented in Table IV.

Table IV. Mulliken Overlap Populations for Acetaldehyde^a

Atom 1	Atom 2	ρ_{12} (H-eclipsing-O)	ρ_{12} (H-eclipsing-H)
C ₁	C ₂	0.46322	0.41908
C ₁	O	-0.15938	-0.13911
C ₁	H ₁	0.75861	0.76302
C ₁	H ₂	0.74345	0.73026
C ₁	H ₃	0.74345	0.76302
C ₁	H ₄	-0.15743	-0.16309
C ₂	O	1.12466	1.09329
C ₂	H ₁	-0.07350	-0.06019
C ₂	H ₂	-0.05209	-0.04986
C ₂	H ₃	-0.05209	-0.06019
C ₂	H ₄	0.78107	0.81203
O	H ₁	0.00783	-0.00164
O	H ₂	0.00155	0.00408
O	H ₃	0.00155	-0.00164
O	H ₄	-0.13351	-0.12952
H ₁	H ₂	-0.03576	-0.04148
H ₁	H ₃	-0.03576	-0.02617
H ₁	H ₄	0.00382	0.00298
H ₂	H ₃	-0.04067	-0.04148
H ₂	H ₄	0.00228	0.00418
H ₃	H ₄	0.00228	0.00298
Atomic charges from population analysis for acetaldehyde ^a			
Atom	H-eclipsing-O	H-eclipsing-H	
C ₁	6.58751	6.58941	
C ₂	5.78991	5.80340	
O	8.35078	8.35049	
H ₁	0.78728	0.78758	
H ₂	0.80796	0.81937	
H ₃	0.80796	0.78758	
H ₄	0.86860	0.86217	

^a All data from ref 7.

(8) R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957).

The results of these and numerous other rotational barrier calculations⁹ unequivocally demonstrate that the origin of rotational barriers is well represented within the Hartree-Fock approximation. For this reason and the fact that, as Moller and Plesset¹⁰ proved, electron densities computed from Hartree-Fock wave functions are accurate to second order,¹¹ it seems reasonable to analyze rotational barriers in terms of their electron-density distributions and distortions derived from accurate *ab initio* wave functions.

The total electron density at a point \vec{r} , $\rho(\vec{r})$, was determined from the formula

$$\rho(\vec{r}) = \sum_i \sum_j |c_{ij}\chi_j|^2$$

where c_{ij} is the molecular orbital coefficient normalized to the proper electron occupancy for the i th molecular orbital and j th normalized atomic orbital, χ_j . The δ function, first defined by Roux, *et al.*¹²

$$\delta(\vec{r}) = \rho_M(\vec{r}) - \rho_A(\vec{r})$$

which represents the difference between the total molecular electron density, $\rho_M(\vec{r})$, and the sum of the juxtaposed atomic densities at \vec{r} , $\rho_A(\vec{r})$, was also utilized. This function has been used extensively to illuminate properties of chemical bonding.² Another Δ function, $\Delta(\vec{r})$, more applicable to rotational barriers, was defined as

$$\Delta(\vec{r}) = \rho_{LS}(\vec{r}) - \rho_E(\vec{r})$$

which yields the difference between the electron density for the less stable conformer, $\rho_{LS}(\vec{r})$, and for the equilibrium configuration, $\rho_E(\vec{r})$, of the rotational barrier at \vec{r} .

In this work, the charge-density-difference diagrams formed from the δ (Δ) functions follow the conventions that a solid contour represents an increase in electron density, a dashed contour indicates a decrease in electron density, and the dotted contours are the lines along which no change occurs. The dotted contours are not shown in all of the difference plots. In the charge-density diagrams, the contours around the atomic centers have been removed for clarity. In all the plots, solid letters correspond to the location of atomic nuclei and dashed letters represent the projections of nuclei onto the plane of the plot. Electron densities are reported in atomic units (1 au = 1 e/a₀³ = 6.7487 e/Å³).

For analyzing chemical bond formation between two atoms with electron-density diagrams, it is obvious that the plots should be made in a plane containing both atoms.² The geometric situation in rotational barriers, however, is not as simple. Our experience has been that for electron-density analyses of rotational barrier molecules, the plane perpendicular to the axis of rotation generally contains the most chemical information of interest.

(9) (a) L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969), presents a summary of *ab initio* calculations on rotational barriers; see also (b) L. C. Allen and H. Basch, manuscript in preparation; (c) R. B. Davidson and L. C. Allen, *J. Chem. Phys.*, in press.

(10) C. Moller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).

(11) That is, the charge distributions obtained in this manner are correct up to the second-order error in a perturbation series representing the difference between the Hartree-Fock solution and the exact wave function.

(12) M. Roux, S. Besnainou, and R. Daudel, *J. Chim. Phys. Physicochim. Biol.*, **53**, 218 (1956).

Results for Ethane

Since the energy difference between eclipsed and staggered ethane represents only $1/20,000$ th of the total molecular energy, a large change in the electronic distributions responsible for the barrier could not be expected. Also, the subtle distortions of charge that would reveal the nature of the barrier might be partially obscured by the large changes in the electronic environment associated with the displacement of the methyl group. Nevertheless, since the ethane barrier is repulsive dominant ($\Delta V_{\text{rep}} > \Delta V_{\text{att}}$), the electron-density distributions in the regions between and around the C-H bonds should show more repulsive character in the eclipsed form than in the staggered. As previously noted,^{9b} although there is greater overlap between the methyl groups in the eclipsed configuration than in the staggered,¹³ the net result is an increase in repulsion between the opposing C-H bonds due to the complete saturation of valence, similar to the interaction between two helium atoms.¹⁴ The purpose of the charge-density analysis was to detect this increase in repulsion, thus verifying the repulsive-dominant nature of the barrier and enhancing its physical presentation.

The total molecular electron-density distribution for eclipsed and staggered ethane in the xy plane, perpendicular to the center of the C-C bond, is shown in Figures 3a and 3b, respectively. These charge-density plots simply reflect the projections of the methyl groups. The threefold symmetry of the eclipsed configuration is readily discernible, while the sixfold symmetry of the staggered configuration is obscured. It is not evident from a comparison of the total molecular charge densities that there is greater repulsion between the methyl groups in the eclipsed form than in the staggered in this plane. The difference plot of the eclipsed minus the staggered electron density in this plane (Figure 3a minus Figure 3b) is presented in Figure 3c. This diagram reveals less electron density between the opposing C-H bonds in the eclipsed configuration than in the staggered, since the negative contours encompass more area than the equivalent areas of charge increase. Thus, Figure 3c indicates greater repulsive character for the interaction between the C-H bonds in the eclipsed form; however, the effect is embedded in the much larger distortion of the electron density created by the physical displacement of the hydrogen atoms.¹⁵

Thus there are two sources contributing to the change in the charge-density distributions as the barrier is traversed. The source producing the largest distortions arises from the change in location of the atomic orbitals. The second source, which is responsible for the more subtle distortions associated with the nature of the barrier, is due to the differences in the molecu-

(13) The increase in overlap is also evidenced by the fact that V_{att} is more negative for the eclipsed form than the staggered.

(14) The He-He repulsion depends, of course, on the Pauli exclusion principle, as has been stated qualitatively for many years [see E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959)]. An especially notable quantitative attempt to determine the exact effects of the Pauli principle on the rotational barrier of ethane has been made by O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968). It is, however, difficult to obtain meaningful results on this question except with charge distributions or total energies because the Pauli principle determines all aspects of shell structure and bonding in such a pervasive manner that it is essentially impossible to separate nonbonded (rotational barrier) effects from direct bonding ones.

(15) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963), report plots similar to Figures 3a-c but do not attempt to analyze them in terms of the barrier mechanism.

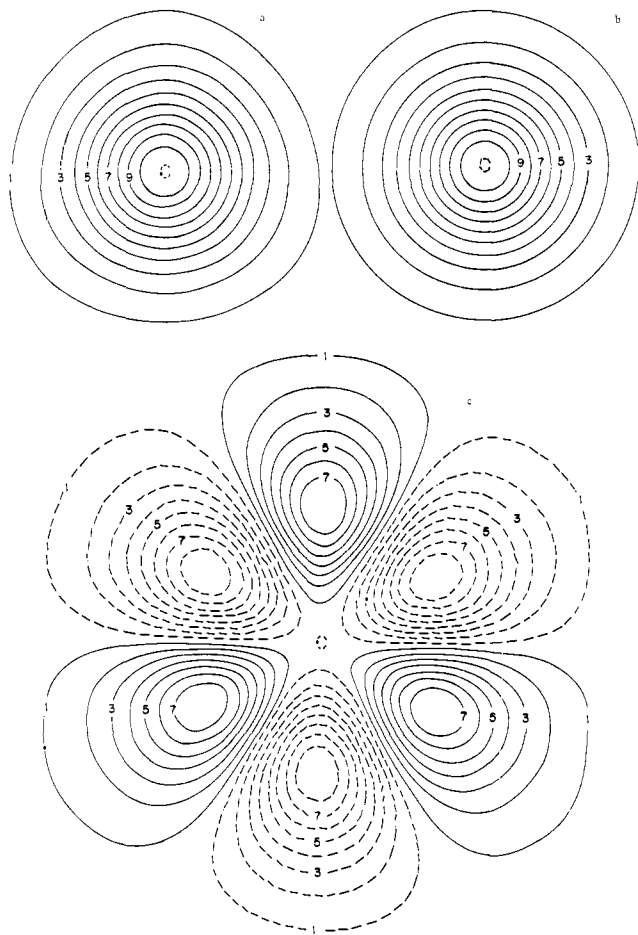


Figure 3. (a) Total charge density for eclipsed ethane perpendicular to the midpoint of the C-C bond. Contour 1 is at 0.018 au and the contour interval is 0.018 au. (b) Total charge density for staggered ethane at the same location as Figure 3a. Contour levels are the same as in Figure 3a. (c) Difference plot of the eclipsed ethane electron density minus the staggered ethane electron density at the same location as Figures 3a and 3b. Contour 1 is at ± 0.0002 au and the contour interval is ± 0.0025 au.

lar orbital coefficients for the two configurations. Naturally, it is the second effect which must be analyzed to obtain the most interesting information concerning the barrier mechanism.

It has been reported¹⁶ and reiterated by Sovers, *et al.*,¹⁴ that there is more gross electronic charge at the center of the C-C bond in eclipsed ethane than in staggered. This result was obtained by the misinterpretation of an electron-density-difference plot for eclipsed minus staggered ethane,¹⁸ where the charge distortion caused by the relocation of the hydrogens in one methyl group due to the rotation was rationalized by more subtle effects. From Figure 3c it can be demonstrated that there is more gross electronic charge at the center of the C-C bond in staggered ethane than in eclipsed. This follows because the areas of charge decrease are larger than the equivalent areas of charge increase caused by rotating from the staggered configuration to the eclipsed. Study of Figure 3 in the work of Pitzer and Lipscomb reveals this same effect in their data. This finding is also supported by the

(16) M. H. Alexander, *J. Chem. Phys.*, **47**, 2423 (1967). Alexander uses and further develops an ingenious model first proposed by Karplus and Parr¹⁷ to approach the barrier problem in ethane.

(17) M. Karplus and R. G. Parr, *ibid.*, **38**, 1547 (1963).

(18) Figure 6 of ref 17.

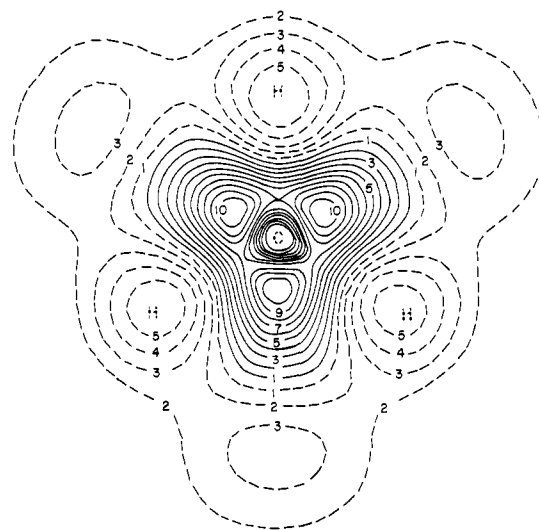


Figure 4. Difference plot of the eclipsed ethane electron density minus the staggered ethane electron density perpendicular to the C-C bond at $Z = 0.5$ au. Contour 1 is at ± 0.00002 au and the contour interval is ± 0.00002 au.

reduction of the C-C overlap population recorded in Table II upon rotation to the eclipsed configuration.

We have attempted to minimize the effect of the relocation of the atomic orbitals by selecting plotting planes far enough from the rotated atoms that the change in the location of their atomic orbitals does not obscure the charge distortions caused by the difference in the molecular orbital coefficients.

The difference plot for the eclipsed ethane electron density minus the staggered in the xy plane at $Z = 0.5$ au is shown in Figure 4, *i.e.*, in the plane perpendicular to the C-C bond and 0.5 au from the carbon atom in the stationary methyl group. This plot clearly shows that an increase in repulsion between the eclipsing C-H bonds is the dominant factor in determining the nature of the ethane barrier. It is seen that there is an electron density decrease in front of the C-H bonds in eclipsed ethane relative to staggered. The repulsive character is also confirmed by the increase in charge directed away from the eclipsing C-H bonds. One would expect that the change due to rotation of the atomic orbitals (on the far methyl rotor) would produce the opposite charge shifts, similar to those in Figure 3c. Thus, the contributions due to the differences in the molecular orbital coefficients for the two conformers determine the areas of electron-density change observed in Figure 4. There is, of course, some cancellation of effects. That is, if the effect of the displacement of the rotated hydrogens were neglected, the decrease in charge between the opposing C-H bonds and the increase in the regions away from them would be larger than indicated in Figure 4. Quantitatively, the amount of charge redistribution would still be small, but again the energy difference between the two conformers relative to the total molecular energy is also very small.

The difference plot for eclipsed minus staggered ethane in the plane 0.5 au behind the hydrogens in the stationary methyl group (the xy plane at $Z = -1.2$) is presented in Figure 5. The contribution due to the change in location of the atomic orbitals at the other end of the molecule is negligible in this plot. Figure 5

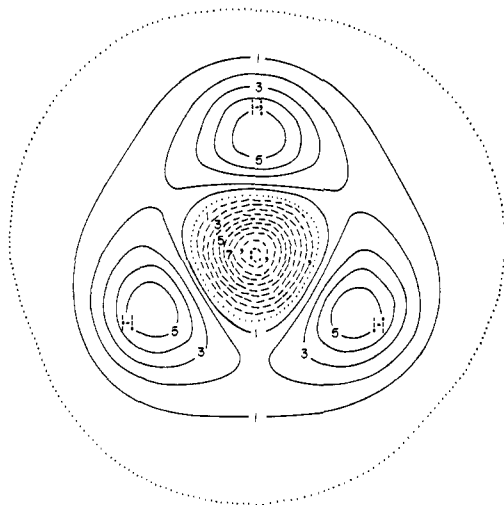


Figure 5. Difference plot of the eclipsed ethane electron density minus the staggered ethane electron density 0.5 au behind the plane of the stationary methyl hydrogens. Contour levels are the same as in Figure 4.

shows that there is more charge behind the stationary hydrogen atoms in eclipsed ethane than in staggered. This results from the increase in repulsion between the eclipsing hydrogens which forces charge behind them. The increased repulsion is confirmed by the decrease in the H_1-H_4 overlap population in Table II. A decrease in electron density behind the carbon atom in the stationary methyl group is also observed in Figure 5 by rotating to the eclipsed configuration. Bader and Henneker² showed that there is a large increase in charge behind carbon atoms forming a good C-C bond as well as in the bonding region between them. The decrease in electron density behind the carbon atoms in eclipsed ethane relative to staggered is, therefore, consistent with the fact that the C-C bond in eclipsed ethane is slightly weaker than in staggered ethane. This is supported by the reduction of C-C overlap population for the eclipsed configuration relative to the staggered.

The completely repulsive nature of a helium-helium interaction at an internuclear separation of 2.0 au is illustrated in Figure 6. The difference plot for the eclipsed ethane electron density minus the staggered in a plane passing through a stationary C-H bond (the yz plane at $x = 0.0$ au) is shown in Figure 7. The interaction between the methyl groups in rotating from staggered to eclipsed ethane follows the same pattern of charge decrease between the centers of repulsion and charge increase behind them observed in the He-He case. This reinforces the analogy between the chemical bonding situation that produces the barrier and the repulsive-dominant interaction of two helium atoms.

By analysis of charge-density distributions, the repulsive-dominant nature of the rotational barrier in ethane has been verified and the physical description of the barrier mechanism expanded, since the charge distortions needed to support the increase in repulsion between the methyl groups in rotating from the staggered configuration to the eclipsed were detected. The charge-density-difference plots emphasize that the origin of rotational barriers lies in the small changes in chemical bonding which accompany the rotation. For

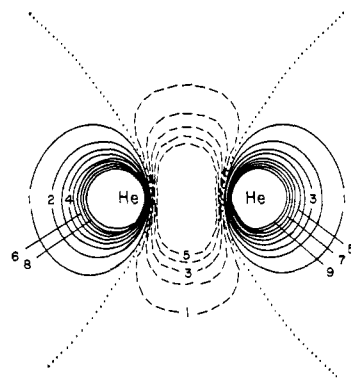


Figure 6. Difference plot of the helium dimer electron density minus the sum of the electron densities of two helium atoms at an internuclear separation of 2.0 au. Contour 1 is at ± 0.002 au and the contour interval is ± 0.004 au.

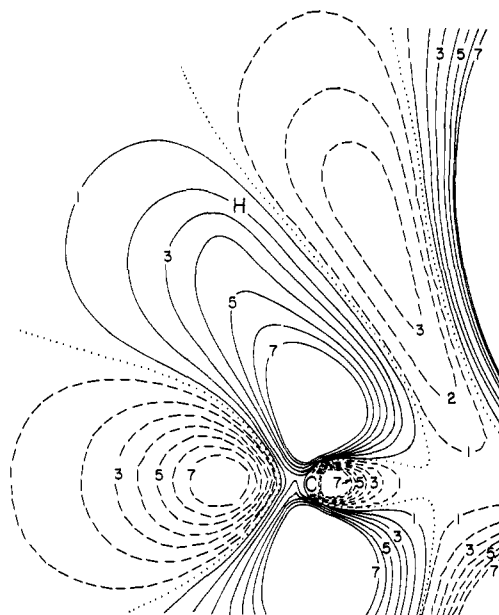


Figure 7. Difference plot for the eclipsed ethane electron density minus the staggered ethane electron density containing the stationary C-H bond in the YZ plane. Contour 1 is at ± 0.00002 au and the contour interval is ± 0.00004 au.

ethane, the charge shifts demonstrate that the barrier is a result of increased repulsion similar to the repulsion of two helium atoms.

Results for Acetaldehyde

Acetaldehyde has been shown to possess a rotational barrier of threefold symmetry that is attractive dominant ($\Delta V_{\text{att}} > \Delta V_{\text{rep}}$), and in contrast to the ethane case, a decrease in attractive interactions rather than an increase in repulsion controls the nature of its barrier. In fact, the repulsive potential, V_{rep} , was found to be more favorable (smaller) in the less stable conformer (H eclipsing H).⁷ Therefore, changes in the electron-density distributions must reflect that a loss of attraction is the predominant effect in rotating from the H-eclipsing-O to the less stable configuration. As in the analysis of the ethane barrier, the charge redistribution caused by the relocation of the atomic orbitals for the methyl hydrogens must be separated from the charge distortions, indicating the change in the chemical bonding which produces the rotational barrier.

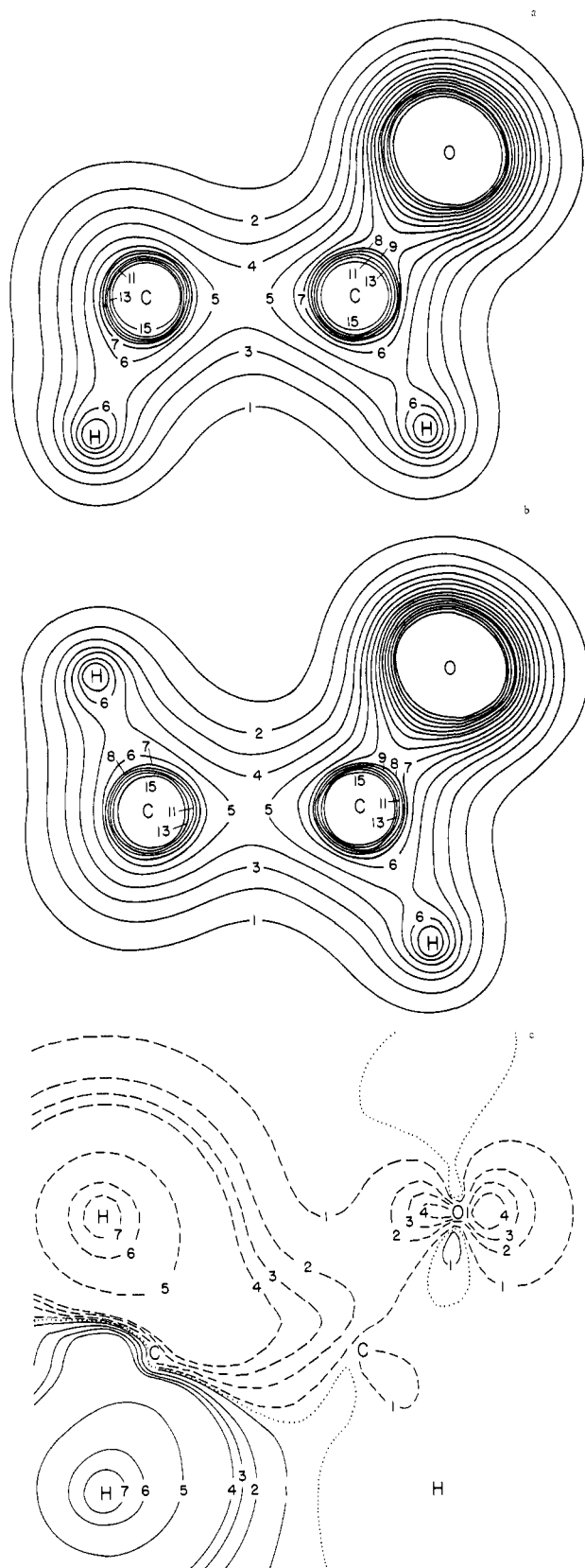


Figure 8. (a) Total charge density for H-eclipsing-H acetaldehyde in the plane of the C-C-O fragment, the YZ plane at $X = 0$. Contour 1 is at 0.05 au and the contour interval is 0.05 au. (b) Total charge density for H-eclipsing-O acetaldehyde at the same location as Figure 8a. Contour levels are the same as in Figure 8a. (c) Difference plot of the H-eclipsing-H acetaldehyde minus the H-eclipsing-O acetaldehyde electron density at the same location as Figures 8a and 8b. The contours are: 1 = ± 0.001 , 2 = ± 0.004 , 3 = ± 0.007 , 4 = ± 0.01 , 5 = ± 0.05 , 6 = ± 0.15 , 7 = ± 0.25 au.

The total molecular electron-density distributions for the H-eclipsing-H and H-eclipsing-O conformers in the plane of the C-C-O fragment are presented in Figures 8a and 8b, respectively. The difference plot of the H-eclipsing-H minus the H-eclipsing-O electron density in this plane is shown in Figure 8c. From the difference plot it is clear that virtually no change in the electron density near the aldehyde hydrogen is caused by the rotation. Thus, the interactions between the methyl group and the aldehyde hydrogen do not contribute significantly to the barrier. The difference plot also reveals a large charge buildup in the region around the oxygen atom and between the C-O double bond and its eclipsing methyl C-H bond in the more stable H-eclipsing-O conformer. In the ethane case, the opposite effect was observed; *i.e.*, there was a charge loss between the C-H bonds when they became eclipsed. The charge increases between the eclipsing bonds and around the oxygen are, therefore, the charge distortions responsible for the attractive dominant nature of the rotational barrier. It is the loss of this highly favorable interaction between the methyl group and the oxygen in the H-eclipsing-O conformer that causes the increase in V_{ne} (less attraction in the H-eclipsing-H configuration) which occurs when the methyl group is rotated to the higher energy configuration. Contrary to the ethane case, it is not an increase in repulsion between the eclipsing C-H bonds that governs the nature of the barrier, but rather a decrease in attraction between the methyl group and the oxygen. The large charge buildup around oxygen results from its high electronegativity, which draws electron density from the methyl hydrogens. These findings are supported by the population analysis in Table IV in which there are positive overlap populations between the oxygen and all of the methyl hydrogens for the H-eclipsing-O conformer, while in the H-eclipsing-H configuration the oxygen only has a positive overlap with the most distant methyl hydrogen. Naturally, part of the charge increase between the C-O double bond and its eclipsing C-H bond is due to the change in location of the methyl hydrogen atomic orbitals. As in the ethane case, this effect decreases rapidly with increase in distance from the rotated hydrogens (the significance of this effect for the analysis of the acetaldehyde barrier will be examined in the next few plots).

The total charge density for H-eclipsing-H and H-eclipsing-O acetaldehyde in the plane perpendicular to the midpoint of the C-C bond (the xz plane at $y = -1.419$ au) is presented in Figures 9a and 9b, respectively. The shapes of these plots reflect the two orientations of the methyl group. The charge-density-difference plot of the H-eclipsing-H minus the H-eclipsing-O configuration in this plane is shown in Figure 9c. It is evident from the difference plot that the charge distortions caused by the relocation of the atomic orbitals are observable in this plane. However, the loss of charge between the C-O double bond and the methyl group, in rotating from the H-eclipsing-O to the H-eclipsing-H configuration, due to the differences in the molecular orbital coefficients, is clearly seen to be the principal effect. The relocation of the methyl hydrogens only contributes to this charge decrease as much as it contributes to the charge increase in the areas of the positive contours.

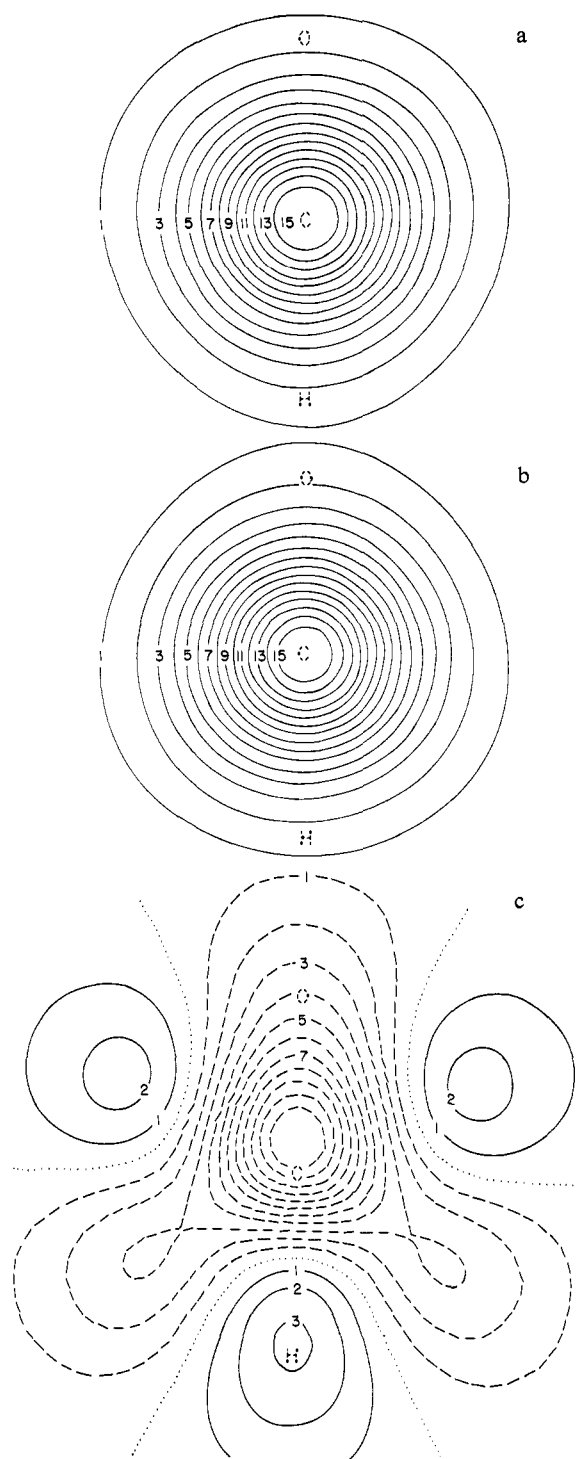


Figure 9. (a) Total charge density for H-eclipsing-H acetaldehyde perpendicular to the midpoint of the C-C bond. Contour 1 is at 0.015 au and the contour interval is 0.015 au. (b) Total charge density for H-eclipsing-O acetaldehyde at the same location as Figure 9a. Contour levels are the same as in Figure 9a. (c) Difference plot of the H-eclipsing-H acetaldehyde minus the H-eclipsing-O acetaldehyde electron density at the same location as Figures 9a and 9b. Contour 1 is at ± 0.001 au and the contour interval is ± 0.001 au.

The charge-density-difference plot for the H-eclipsing-H conformer minus the H-eclipsing-O conformer in the plane perpendicular to the C-C bond ($y = -0.709$ au) is presented in Figure 10. This plane intersects the C-C bond halfway between the midpoint of the bond and the aldehyde carbon. The contribution to the charge den-

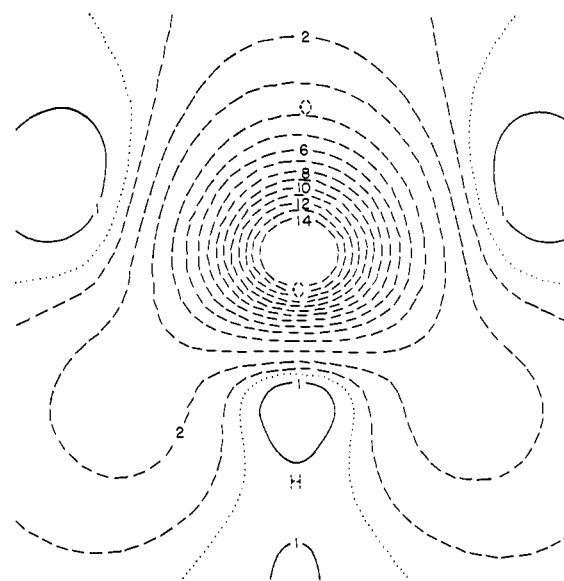


Figure 10. Difference plot of the H-eclipsing-H acetaldehyde minus the H-eclipsing-O acetaldehyde electron density perpendicular to the C-C bond and halfway between the midpoint of the bond and the aldehyde carbon. The contour levels are: 1 = ± 0.0001 , 2 = -0.0003 , 3 = -0.0006 au. The contour increment for the contours greater than 3 is -0.0005 au.

sity due to the change in position of the atomic orbitals for the methyl hydrogens is very small, as indicated by the presence of the sole positive contour. Again, the loss of the favorable interaction between the oxygen and the methyl group in rotating to the H-eclipsing-H configuration appears as the overwhelming contributor to the attractive-dominant nature of the barrier.

From these last two difference plots (Figures 9c and 10), it is evident that consideration of the contribution to the total electron density from rotating the methyl hydrogen atomic orbitals is not as significant in examining the barrier in acetaldehyde as it was in ethane. This makes the charge-density analysis of the acetaldehyde barrier more straightforward. Nevertheless, it is still best to analyze the electron-density distributions in planes perpendicular to the rotation axis that are at least 2.5 au from the plane of the rotated hydrogens.

The inadequacy of population analyses to properly represent heteroatomic intermolecular interactions is accentuated by the finding that the gross atomic charge from population analysis on oxygen in Table IV is virtually the same in both configurations of acetaldehyde. The charge-density-difference plots demonstrate that there is noticeably more charge on oxygen in the H-eclipsing-O than in the H-eclipsing-H conformer.¹⁹ The population analysis also indicates a charge buildup on the aldehyde carbon in rotating to the H-eclipsing-H configuration. The difference plots reveal that there is actually less electron density surrounding the aldehyde carbon in the H-eclipsing-H conformer than in the H-eclipsing-O conformer. In fact, the lone area of charge increase in rotating to the H-eclipsing-H configuration is around the methyl hydrogen which eclipses the aldehyde hydrogen (see Figure 8c). The total charge density for the H-eclipsing-H conformer in the plane passing through the nuclei of the methyl hydrogens is shown in

(19) A precise number for the electronic charge cannot be meaningfully obtained from the charge-distribution plots because it requires the assignment of a specific volume of integration which is itself arbitrary.

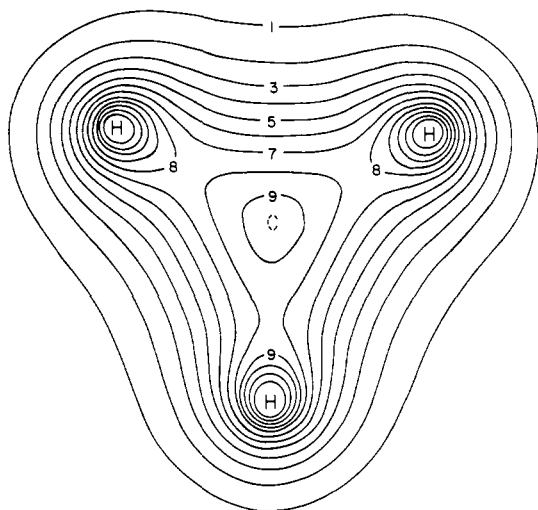


Figure 11. Total charge density for H-eclipsing-H acetaldehyde in the plane of the methyl hydrogens. Contour 1 is at 0.03 au and the contour interval is 0.03 au.

Figure 11. The increased electron density in the vicinity of the unique methyl hydrogen relative to the two equivalent methyl hydrogens is substantiated by this plot.

The attractive-dominant nature of the rotational barrier in acetaldehyde has been confirmed by the analysis of charge-density distributions. The dominating effect in determining the nature of the barrier is observed to be the loss of the attractive interaction between the oxygen and the methyl group when rotation to the less stable, H-eclipsing-H configuration occurs. These findings again emphasize that the origin of rotational barriers is in small-scale changes in ordinary chemical bonding. The charge-density-difference plots reveal charge increase in the region between the oxygen and its eclipsing hydrogen and polarization of that hydrogen's charge toward the oxygen in the equilibrium conformation. This is consistent with the formation of a weak covalent bond between the oxygen and the methyl hydrogen that eclipses it in this conformation.²⁰ These charge-density shifts are analogous to those associated with formation of the ordinary covalent bond in OH.²¹ This is further supported by the charge increase on the oxygen and the charge decrease on the eclipsing hydrogen evident from population analysis²² and the increase in charge between them reflected in the H₁-O overlap population increase (Table IV). These are the same directions of change found from population analysis of the

(20) In an earlier paper⁴ the concept of repulsive and attractive dominant barriers was introduced, and the barrier energy components were shown to parallel those of the typical and well-understood conventional bonding in He₂ and H₂. These molecules are the standard textbook representatives of the two most general classes of atomic interactions, and the purpose was to point out that in the list of known barriers there were examples of *attractive-dominant* as well as *repulsive-dominant* cases. For attractive-dominant cases it is to be expected that an increase in charge density in one particular region will generally control the barrier, and this obviously suggests analogy to the appropriate diatomic molecules. Thus we give a reference below to a charge-density-difference map for OH. However, a charge-density analysis has not been carried out for any other attractive-dominant barrier, so we cannot determine whether or not analogy to a more specific diatomic than H₂ will yield appreciably more information.

(21) Figure 3 (p 3387) of ref 1. Of course the equilibrium distance in diatomic OH is 1.83 au, while the OH bonded separation in acetaldehyde is 4.7 au, but the attractive nature of the OH interaction and the tendency to shift charge from H to O is present at separations even beyond 4.7 au.

(22) As noted above, the population analysis underestimates the actual charge shift on the oxygen appearing in the difference plots.

ordinary OH covalent bond. The attractive-dominant nature of the rotational barrier in acetaldehyde can be considered to result from the dissolution of this weak covalent bond upon rotation to the less stable conformer.

Finally, it may be important to record that the C-C overlap population in ethane decreased by 0.012 and in acetaldehyde by 0.044 as the barriers were traversed from their low- to high-energy conformations. Changes of this magnitude have also been observed recently for nitrosomethane,^{23a} propene,^{23b} *cis*-fluoropropene,^{23b} *trans*-fluoropropene,^{23b} and hydrogen peroxide,^{23c} where in every case the lowest energy configuration has the largest overlap population for the bond about which the rotation occurs.

Summary and Conclusions

This study demonstrates that the rotational barriers' repulsive- or attractive-dominant nature which characterizes their origin can be detected and elucidated by analysis of charge-density distributions. It is necessary that the LCAO-MO-SCF wave functions from which the charge-density plots are derived be reasonably near to molecular Hartree-Fock solutions.^{3a} The theory of rotational barriers derives great benefit from this form of analysis because changes in a pictorially represented physical property, rather than a computed number, are being scrutinized.

For the ethane barrier, it was found that the principal charge shifts accompanying the rotation from the more stable, staggered configuration to the eclipsed configuration are a decrease in charge between the eclipsing C-H bonds and increases behind the hydrogen nuclei and directed away from the eclipsing bonds. These shifts exhibit the increase in repulsion between the C-H bonds as they become eclipsed, which is consistent with the repulsive-dominant nature of the barrier.

For the acetaldehyde barrier, the loss of the highly favorable interaction between the oxygen and the methyl group in rotating from the H-eclipsing-O conformation to the less stable H-eclipsing-H conformation was shown to give the barrier its attractive-dominant character. The barrier mechanisms for the two molecules are conveniently contrasted by noting that the repulsive dominance of the ethane barrier is due to the eclipsing C-H bonds interacting like two helium atoms, while the attractive dominance of the acetaldehyde barrier is a result of the weak covalent bond formed between the oxygen and its eclipsing methyl hydrogen.

These results establish that the origin of the hindering potential for rotations around single bonds is found in small changes in the chemical bonding which can be identified with charge-density analysis.

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(23) (a) P. A. Kollman and L. C. Allen, *Chem. Phys. Lett.*, **5**, 75 (1970); (b) E. Scarzafava and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 311 (1971).