J. Am. Chem. Soc. 1993, 115, 1074–1078

An ab Initio CASSCF Study of δ Bonding in the $Mo_2Cl_4(PH_3)_4$ Molecule

F. Albert Cotton* and Xuejun Feng

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. *Received July 8, 1992*

Abstract: The properties of the δ bond in the $Mo_2Cl_4(PH_3)_4$ species have been studied by calculations using ab initio CASSCF wave functions in conjunction with effective core potentials. The energies of the ground state and the first two excited states of the δ manifold have been calculated as a function of the angle of internal rotation. The results can be compared with experimental results for a series of molecules of $M_2X_4(LL)_2$ type in which the steric requirements of the LL ligands introduce various angles of internal rotation away from the eclipsed conformation. For the separation between the singlet ground state and the triplet first excited state the results are in good agreement with those experimentally obtained. The singlet δ–δ^* transition energies given by our calculations display a nearly constant discrepancy over the full range of the internal rotation when compared with the spectroscopic results, but this is consistent with the expected atomic intrapair correlation energy for the highly ionic singlet excited state. The δ-bond energy is estimated to be 16.8 kcal mol^{-1} and the calculated electronic contribution to the barrier of internal rotation is 12.4 kcal mol^{-1}.

Introduction

Since the discovery of the quadruple bond in 1964,[1] numerous studies, both theoretical and experimental, have been devoted to the field of multiple bonding between metal atoms.[2,3] A point of particular interest is that the δ bond became for the first time a subject not only available for thorough and exacting experimental investigation but worthy of detailed theoretical attention.[4]

In terms of molecular orbital description, the δ bond in a quadruply bonded species is formed with a double occupation of the δ bonding orbital which is derived from positive overlap of the atomic dδ orbitals. The overlap and hence the strength of the δ bond are a function of cos 2χ where χ is an average torsional angle away from an eclipsed conformation in which $\chi = 0°$.[2] As a result, the strength of the δ bond is particularly sensitive to the angle χ, in addition to its dependence on metal–metal bond distance. Thus from a maximum at $\chi = 0°$, the δ-bond strength will decrease, slowly at first, until it becomes annihilated at $\chi = 45°$. The special feature of the δ bond, namely, its angle-sensitivity, affords us another opportunity, by a means other than dissociation, to study the behavior of a chemical bond as it approaches extinction.

It has been found[5] that we can, by doing chemistry, create a series of compounds of $M_2X_4(LL)_2$ type, where LL is a bidentate phosphine ligand, in which the torsional angle is changed in fairly small increments from $\chi = 0°$ to 40° while practically nothing else is changed. These twists lead to a decrease in the singlet δ–δ^* transition energy[5] and a lengthening of the M–M distance,[6] both indicating a weakening of the δ bond. In recent work employing an NMR technique,[7] the energy differences between the singlet ground state and the triplet first excited state (singlet–triplet separation) of the systems were also measured accurately as a function of the twist angles. The results have established, for the first time, the accurate δ-bond energy and the δ barrier. Prior to this new development, there was only one reported case based on magnetic measurement, and only a crude result was obtained.[8]

Compared to the theoretical efforts to understand electronic structure of the ground state in the quadruply bonded systems,[2,3] specific investigations by ab initio methods into the δ bond and the excited states, particularly those of the δ manifold, have received less attention. The first treatment of the δ bond was given by Hay[9] in his pioneering and comprehensive GVB-CI calculations on both ground state and excited states of $[Re_2Cl_8]^{2-}$. Electronic transitions from the ground state to a number of excited states were also calculated for two dimolybdenum compounds, $[Mo_2Cl_8]^{4-}$ and $Mo_2(O_2CH)_4$, by the CASSCF method.[10] The rotation barrier obtained in these calculations for the unbridged ions, however, is either very unsatisfactory[9] or even qualitatively incorrect.[10] In a recent study, again, on the $[Re_2Cl_8]^{2-}$ ion by Smith and Goddard,[11] the lowest two electronic states were calculated as a function of the rotation angle, using a modified-GVB (MGVB) method. Their results for the δ-bond strength and the singlet–triplet energy separation in this ion are certainly reliable and ought to be accurate. Unfortunately, it is not for this type of system that experimental data on twisted molecules are available and, therefore, direct comparison with experimental results is impossible.

We report here the results of our ab initio CASSCF calculations on the $Mo_2Cl_4(PH_3)_4$ molecule. Such a molybdenum system is a very attractive subject for a theoretical study of the δ bond because of the existing experimental data and relatively small spin–orbit coupling effects compared to the case of the rhenium compound. We have calculated not only the ground state but also the first two excited states of the δ manifold, all as a function of the angle of internal rotation. The calculated singlet–triplet energy separations were then used to estimate the δ-bond energy and the δ contribution to the rotational barrier. Calculated results for the singlet δ–δ^* transition energies are also to be discussed. The theoretical results will then be compared with the experimental results obtained for molecules of the $Mo_2Cl_4(PP)_2$ type.

Computational Details

The calculations were performed by the complete active space SCF (CASSCF) method[12] on a model molecule, $Mo_2Cl_4(PH_3)_4$. The structural parameters were based on the crystal structure of $Mo_2Cl_4(PMe_3)_4$[13] which has a strictly eclipsed conformation and has D_{2d} symmetry. The bond distances and angles used are as follows: Mo–Mo = 2.130 Å, Mo–Cl = 2.414 Å, Mo–P = 2.545 Å, Mo–Mo–Cl = 112.22°, and Mo–

---

[1] Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334.

[2] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

[3] Cotton, F. A.; Walton, R. A. *Struct. Bonding* **1985**, *62*, 1.

[4] Cotton, F. A. *Pure Appl. Chem.* **1992**, *64* (No. 10), 1383.

[5] Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 177.

[6] Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 4384.

[7] Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915. A full report is in preparation.

[8] Hopkins, M. D.; Zietlow, T. C.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 510.

[9] Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7007.

[10] (a) Mathisen, K. B.; Wahlgren, U.; Pettersson, L. G. M. *Chem. Phys. Lett.* **1984**, *104*, 336. (b) Stromberg, A.; Pettersson, L. G. M.; Wahlgren, U. *Chem. Phys. Lett.* **1985**, *118*, 389.

[11] Smith, D. C.; Goddard, W. A., III *J. Am. Chem. Soc.* **1987**, *109*, 5580.

[12] (a) Jonsson, B.; Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *J. Chem. Phys.* **1981**, *74*, 4566; (b) Knowles, P. J.; Sexton, G. J.; Handy, N. C. *Chem. Phys.* **1982**, *72*, 337.

[13] Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

0002-7863/93/1515-1074$04.00/0

Mo–P = 102.32°. The same parameters were used for all of the following angles (χ) of internal rotation: 0°, 15°, 25°, 35°, 45°, 55°, 65°, 75°, and 90°. The angle, χ, here is defined in a way different from that mentioned earlier as will be discussed below.

The calculations utilized effective core potentials (ECP) so that only the outermost electrons of each atom were treated explicitly. For molybdenum, these include electrons in the 4s, 4p, 4d, and 5s orbitals, and for chlorine and phosphorus these are the 3s and 3p electrons. We used the ECPs of Hay and Wadt[14] and their valence Gaussian basis sets. For Mo, the (5s5p4d) basis set was contracted to a (3s3p3d) basis set. Thus our resulting d basis is of triple-ζ quality. For a good description of electronic states of transition metal compounds of this type, it appears that a triple-ζ quality d basis is required. For both Cl and P, the (3s3p) basis set was contracted to a double-ζ (2s2p) set. For hydrogen, a single-ζ basis function consisting of a set of four primitive Gaussian functions of Huzinaga[15] was used.

The CASSCF wave function for each electronic state studied was constructed by distributing eight d electrons among the eight M–M bonding and antibonding orbitals, namely, the σ, π, and δ orbitals and their antibonding counterparts. Therefore, we have a full CI wave function within the full quadruple bond manifold. All other orbitals were kept either frozen or inactive. The number of configuration state functions varied between 470 and 600.

All calculations were carried out with the GAMESS program[16] and on a CRAY Y-MP2 computer at the Texas A&M University Supercomputer Center.

Electronic States of the δ Manifold

It is well-known that the ground state electronic configuration in a quadruply bonded system can be designated as $\sigma^2\pi^4\delta^2$. In such a system the δ orbital is the HOMO and there is a low-lying LUMO, the antibonding δ^* orbital, as a result of relatively weak δ interaction. For a system with D_{4h} symmetry, the electronic states derived from the δ^2, $(\delta\delta^*)^2$, and $(\delta^*)^2$ electronic configurations are $^1A_{1g}$, $^3A_{2u}$ and $^1A_{2u}$, and $^1A_{1g}{}^*$ (the δ manifold), respectively. The relative energies of these states have been shown[9] to be in the following order, $^1A_{1g} < {}^3A_{2u} \ll {}^1A_{2u} < {}^1A_{1g}{}^*$, instead of an intuitively expected order by simply considering the δ bonding, namely, $^1A_{1g} \ll {}^3A_{2u} < {}^1A_{2u} \ll {}^1A_{1g}{}^*$.

The limiting behavior of the δ manifold and the δ bond may be studied by considering bond stretching as in an isolated two-center two-electron system. The general problem, as embodied by the particular case of the bond in the hydrogen molecule, was addressed by Coulson and Fischer[17] a long time ago. The treatment when adapted for the δ bond has given a conceptually clear and simple picture of the δ manifold as a function of internuclear distances.[2,18] However, in reality we cannot experimentally measure the properties of a δ manifold as the internuclear distances increase toward the dissociation limit. Theoretical treatment of a high accuracy is also difficult because all components of a quadruple bond will be stretched simultaneously to extinction. Only limited studies on the δ-bond strength using this approach have been reported.[19]

Another way to manipulate the strength of the δ bond is to take advantage of the sensitivity of the bond to internal rotation and to twist the bond. It is worth noting that the σ and two π components of a quadruple bond will not be affected by the twisting because of their overall cylindrical symmetry about the metal–metal axis. Thus, by calculating or measuring the energies or energy differences, particularly between the ground state $^1A_{1g}$ and the first excited state $^3A_{2u}$, as a function of the angle χ, the δ-bond strength can be very well established, as we have already mentioned earlier.

Twisting the δ bond resembles stretching the bond only in the sense that in both cases the δ bond is weakened and then annihilated at the limits of the processes. Otherwise, they have little in common. A very obvious difference is that while it is rigorously true that when the δ bond is annihilated by stretching it, the two lower states ($^1A_{1g}$ and $^3A_{2u}$) and the two upper states ($^1A_{2u}$ and $^1A_{1g}{}^*$) will converge,[18] this need not be the case when the bond is annihilated by twisting it. As a matter of fact, the $^1A_{1g}$ state is always lower than the $^3A_{2u}$ state when the bond is twisted as it has been shown in molecules of the M_2X_8 type[9,11] and as it will be seen later for the $Mo_2Cl_4(PH_3)_4$ molecule. It is clear that at the stretching limit we are dealing with a dissociated system that consists of two non-interacting fragments, while the entire twisting process only involves an internal rotation.

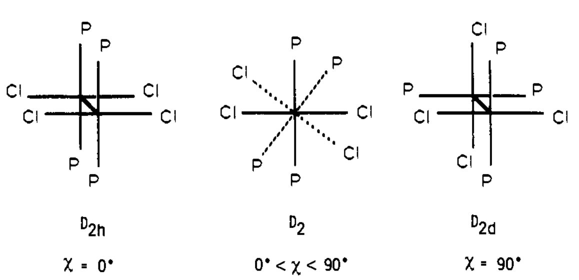

Figure 1. Definition of the internal rotation angle in $Mo_2Cl_4(PH_3)_4$ and symmetries of different conformations.

Table I. Correlation of Electronic States of the δ Manifold

	D_{4h}	D_{2h}	D_2	D_{2d}
$^1\delta^2$	$^1A_{1g}$	^1A_g	^1A	$^1A_1$
$^3\delta\delta^*$	$^3A_{2u}$	$^3B_{1u}$	$^3B_1$	$^3B_2$
$^1\delta\delta^*$	$^1A_{2u}$	$^1B_{1u}$	$^1B_1$	$^1B_2$
$^1\delta^{*2}$	$^1A_{1g}{}^*$	$^1A_g{}^*$	$^1A^*$	$^1A_1{}^*$

Let us reiterate for emphasis that a very important reason for carrying out the calculations reported here is that there are experimental results with which the calculated results may be compared. While calculations concerning the effects of stretching the bond may be interesting in some ways, they are ultimately sterile because the well-known lack of molecular tweezers makes it impossible to obtain the corresponding experimental data. Similarly, calculations of the effect of twisting the $M_2X_8{}^{n-}$ type systems also produce results that are not testable against experiment.

As an M_2X_8 system is twisted from the eclipsed conformation ($\chi = 0°$) the symmetry changes from D_{4h} to D_4 and then becomes D_{4d}. Throughout the range of intermediate configurations, the two dδ atomic orbitals continue to interact to form bonding δ and antibonding δ^* MOs, but at the 45° limit their overlap becomes zero and they become rigorously degenerate, forming a basis for the E_2 representation of the D_{4d} point group. The $e_2{}^2$ configuration gives rise to four separate electronic states, namely, $^1B_1$, $^3A_2$, $^1B_2$, and $^1A_1$. These states may be correlated with the intermediate D_4 states, $^1A_1$, $^3A_2$, $^1A_2$, and $^1A_1{}^*$, which in turn correlate to the D_{4h} states, $^1A_{1g}$, $^3A_{2u}$, $^1A_{2u}$, and $^1A_{1g}{}^*$, respectively. For the molecule under current consideration, $Mo_2Cl_4(PH_3)_4$, the situation is slightly different. There are now two different eclipsed conformations, of D_{2h} and D_{2d} symmetries, as shown in Figure 1. We may start from either conformation and twist the molecule to the same staggered conformation. In our calculations we have defined the angle of internal rotation in a way different from the one commonly used[2] in which χ is an averaged torsional angle away from an eclipsed conformation. The angle, χ, is defined here as the dihedral angle P–Mo–Mo–P and varies in a range from 0° to 90°. Thus at $\chi = 0°$ and 90°, the molecule has D_{2h} and D_{2d} symmetries, respectively, and all intermediate conformations have D_2 symmetry (Figure 1). The correlation of the states of the δ manifold in different symmetries is shown in Table I. Throughout the following discussion, for simplicity, the electronic states of the δ manifold will be designated as $^1\delta^2$, $^3\delta\delta^*$, $^1\delta\delta^*$, and $^1\delta^{*2}$, even though this is clearly not applicable in the case when $\chi = 45°$.

Single–Triplet Separation

The results of the CASSCF calculations for the energy differences between the ground state, $^1\delta^2$, and the first excited state,

---

(14) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270, 284, and 299.

(15) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(16) Guest, M. F. *GAMESS User's Guide and Reference Manual*; Daresbury Laboratory, 1989.

(17) Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386.

(18) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. *Polyhedron* **1987**, *6*, 705.

(19) Ziegler, T.; Tschinke, V.; Becke, A. *Polyhedron* **1987**, *6*, 685 and references therein.

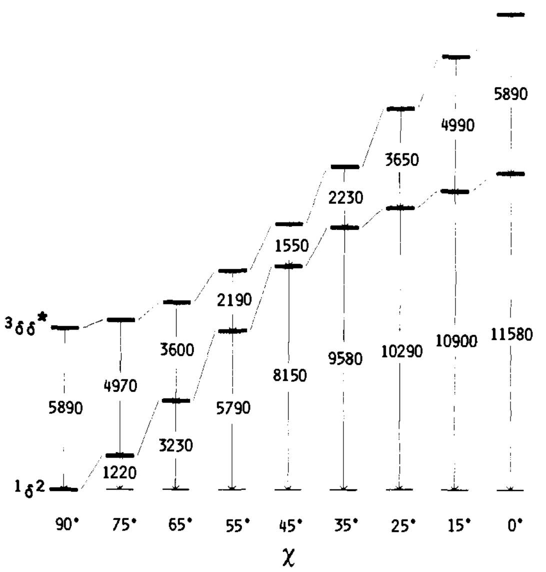

Figure 2. Calculated energies (cm^{-1}) of the $^1\delta^2$ and $^3\delta\delta^*$ states of $Mo_2Cl_4(PH_3)_4$ and their energy differences (cm^{-1}) as a function of the angles of internal rotation.

$^3\delta\delta^*$, in $Mo_2Cl_4(PH_3)_4$ are shown in Figure 2 as a function of the rotation angle χ. A notable feature of the calculated energies is that the singlet $^1\delta^2$ state is always lower than the triplet $^3\delta\delta^*$ state, particularly at $\chi = 45°$ where the δ bond no longer exists. This is exactly the same result as that calculated for $[Re_2Cl_8]^{2-}$,[9,11] and it is distinct from that when the bond is stretched to the dissociation limit.

As shown in Figure 2, both singlet and triplet states of the D_{2d} eclipsed conformation ($\chi = 90°$) have the lowest energy, indicating that the conformation is the most stable one. This is an expected result since it is in agreement with the experimentally observed structural preference. As the molecule is twisted away from this eclipsed conformation in which the δ bond has the maximum strength, the energies of the two states both increase, but there is a steady decrease in the energy difference. At the staggered conformation ($\chi = 45°$) where the δ bond ceases to exist, the energy separation becomes minimal. Thereafter, the state energies continue to increase, but the difference gradually becomes larger until the molecule becomes again eclipsed, but with D_{2h} symmetry, at $\chi = 0°$. It is interesting to see that the energy differences are about the same at the two angles χ_1 and χ_2 which satisfy the relation $\chi_1 - 45° = 45° - \chi_2$, that is, the two angles giving equal differences from the two different eclipsed conformations. The symmetric pattern of the energy differences about $\chi = 45°$ simply indicates that, as would be expected, the δ bond strength is essentially only a function of conformational changes from eclipsed to staggered and is independent of choice of the starting eclipsed conformation in the type of molecules under consideration.

The energy change in the ground state $^1\delta^2$ should involve only two major contributions, namely, changes in δ bonding and changes in the interactions between nonbonded atoms, namely, electrostatic and steric interactions between the ligands bonded to opposite metal atoms. It should be pointed out that the change in the electrostatic and steric repulsions as a result of the internal rotation in $Mo_2Cl_4(PH_3)_4$ is very different from that in the D_{4h} systems such as $[Re_2Cl_8]^{2-}$. In the latter case, rotating from eclipsed ($\chi = 0°$) to staggered ($\chi = 45°$) will reduce these repulsions to a minimum, and further rotation to $\chi = 90°$ is simply a mirror-image process that brings the system back to an indistinguishable eclipsed conformation. In $Mo_2Cl_4(PH_3)_4$, however, the minimum repulsion occurs at the D_{2d} eclipsed conformation ($\chi = 90°$), where the bulky phosphine ligands on the opposite Mo atoms are most separated. At the D_{2h} eclipsed conformation ($\chi = 0°$) in which all phosphines on the opposite Mo atoms face each other, the repulsions become strongest. From $\chi = 90°$ to 45°, the energy of the $^1\delta^2$ state increases rapidly since this is a combined result of loss of the δ bonding energy and rise in the electrostatic and steric repulsions. From 45° to 0°, on the other hand, the rise of the repulsions is offset by regaining of the δ bonding energy and, therefore, the energy increase becomes much slower.

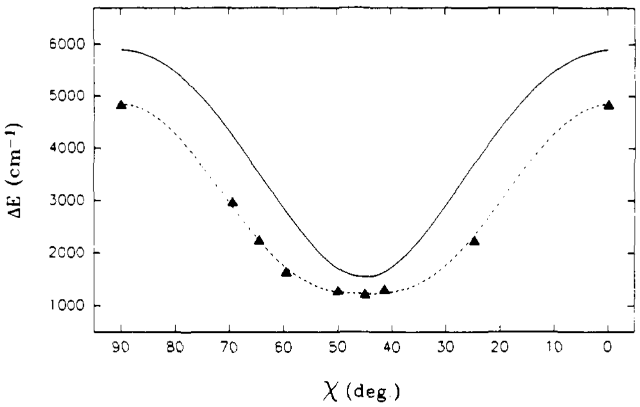

Figure 3. Comparison of the singlet–triplet separations as a function of the internal rotation angles: (—) calculated results for $Mo_2Cl_4(PH_3)_4$; (---) from a nonlinear least-square fitting of the measured results (triangles) for molecules of the $Mo_2Cl_4(PP)_2$ type.

For the triplet $^3\delta\delta^*$ state with two unpaired electrons in each of the δ and δ^* orbitals, the energy increase, starting from $\chi = 90°$, may be attributed mainly to the increase in the repulsions. This is also consistent with the pattern of energy increase of the state as shown in Figure 2. As the rotation proceeds, the phosphine ligands bonded to one Mo atom are getting away from the Cl atoms bonded to the other Mo atom, but at the same time they are moving closer to the phosphine ligands bonded to that Mo atom. Therefore, when the rotation angle is not very far from 90° the net increase of the repulsions is small and the state energy is only raised slightly. As the rotation continues, however, the repulsions between the phosphine ligands become increasingly strong and the energy of the $^3\delta\delta^*$ state rises rapidly.

In Figure 3 the calculated singlet–triplet energy separations are compared with the experimentally measured values for molecules of the $Mo_2Cl_4(PP)_2$ type.[7] As can be seen from the figure, the theoretical result for the energy separation as a function of the rotation is not only qualitatively in very good agreement with the experimental result but also quantitatively comparable. It is noted that around $\chi = 45°$ the calculated values have their best quantitative agreement with the measured ones, but away from that region the discrepancies become larger, maximizing at about 1200 cm^{-1}. The discrepancies may be in part due to the fact that the model molecule used for the calculations, though, very similar, is still different from the molecules on which the measurements were made. However, it is also essential to recognize that all calculations, for both states, were carried out at a fixed nuclear geometry except for changes in the internal rotation angle. For example, at the D_{2d} eclipsed conformation, the energies of both states were calculated with Mo–Mo = 2.13 Å.

But the energy separation so calculated for an eclipsed molecule at fixed Mo–Mo distance must deviate from the result that is obtained for each state at its equilibrium geometry which would correspond to the measured result. For a conformation in which a full or a partial but still significant δ bond exists, the singlet state is a δ bonded state and the triplet state should be δ nonbonded. Therefore, the potential curves of the two states as a function of the Mo–Mo distances must be different from each other, and the minimum in each curve must occur at different Mo–Mo distances. In the region close to the staggered conformation, it is reasonable to expect, conversely, that the equilibrium Mo–Mo distances for the two states would be very similar and the potential curves would be nearly parallel to each other around the equilibrium distances.

With these considerations in mind, we calculated the potential energy as a function of the Mo–Mo distances for the $^1\delta^2$ and $^3\delta\delta^*$ states at both D_{2d} eclipsed conformation ($\chi = 90°$) and the staggered conformation ($\chi = 45°$). As shown in Figures 4 and 5, the results are very much as expected. In the eclipsed case

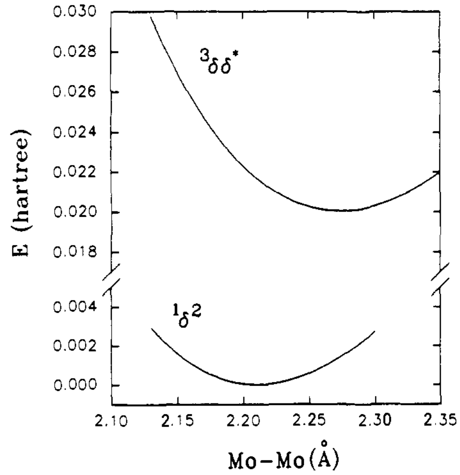

Figure 4. Calculated potential curves for $Mo_2Cl_4(PH_3)_4$ in the $^1\delta^2$ ($^1A_1$) and $^3\delta\delta^*$ ($^3B_2$) states both at the D_{2d} eclipsed conformation (χ = 90°).

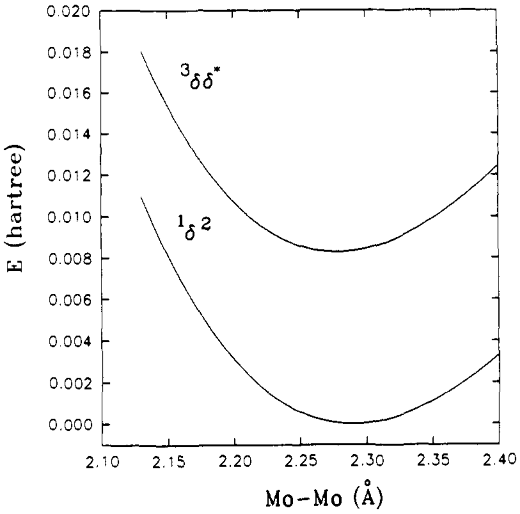

Figure 5. Calculated potential curves for $Mo_2Cl_4(PH_3)_4$ in the $^1\delta^2$ (^1A) and $^3\delta\delta^*$ ($^3B_1$) states both at the staggered conformation (χ = 45°).

(Figure 4), the calculated Mo–Mo distance is 2.210 Å for the ground state and 2.275 Å for the next higher triplet state. The energy separation of the states at these distances is 4400 cm^{-1}, as compared to 4840 cm^{-1} extrapolated from the measured values by a nonlinear least-square curve fitting,[7] and compared to 5890 cm^{-1} calculated at the fixed distance (2.13 Å). Figure 5 illustrates the potentials of the two states at the staggered conformation. The equilibrium Mo–Mo distances are 2.29 and 2.28 Å for the singlet and the triplet states, respectively. The potential curve of one state is indeed not very far from being parallel to that of the other state.

Another way to look at the approximately 1200-cm^{-1} discrepancy between the singlet–triplet separation calculated at a fixed Mo–Mo distance and the measured value is this. In the triplet state the molecule would be in an excited vibrational state when at the same Mo–Mo distance as that characteristic of the singlet ground state. From numerous studies[2] of the Franck–Condon factors for $^1A_{2u} \leftarrow {}^1A_{1g}$ transitions we can estimate that the vibrational excitation would be to about the 3rd level. With $\nu \simeq$ 400 cm^{-1} [2] for typical $Mo_2X_8^{4-}$ or $Mo_2X_4L_4$ compounds, the calculated "vertical" excitation energy would thus be *expected* to exceed the actual value by about $3\nu \simeq$ 1200 cm^{-1}. Thus, there is actually quite good agreement between the calculated and the observed singlet–triplet energies.

δ-Bond Energy and δ Barrier

Our calculations enable us to provide quantitative estimates of these quantities *provided* we first define them. We have made the following choices for these definitions. The δ-bond energy is defined as the least costly way to annul the δ bond within the fixed molecular geometry. The δ barrier, on the other hand, corresponds to the least rise in energy due entirely to loss of the δ bonding from an eclipsed conformation to the staggered one.

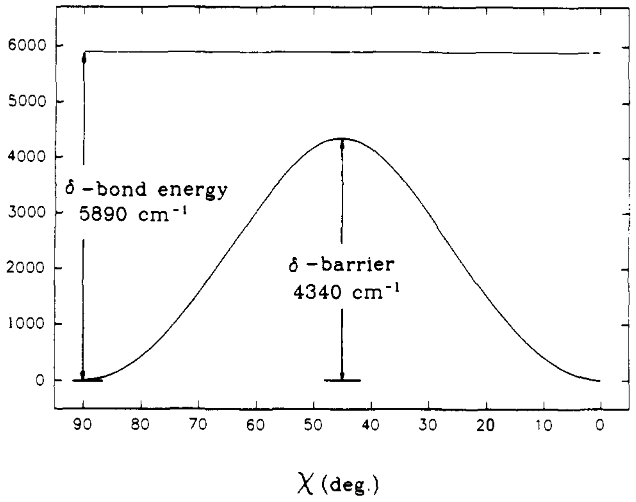

Figure 6. Calculated plot of the δ-bond energy and δ barrier.

The δ-bond energy could, perhaps, have been taken as equal to the δ barrier as some authors have explicitly or implicitly done. We prefer to call the singlet–triplet energy difference at χ = 90° (or 0°) the δ-bond energy. This seems justified since it is the rise in energy when we simply change from the spin-paired ground state to the nearest state in which the spins are parallel. To obtain the δ barrier (see also Figure 2), we take the energy of the $^3\delta\delta^*$ states at χ = 90° as a reference and then subtract the energy increase in the triplet state from the energies of both singlet and triplet states at each of all other angles. The results are shown in Figure 6. Thus, our calculations, using fixed bond distances and angles except χ, predict the δ-bond energy and the δ barrier in $Mo_2Cl_4(PH_3)_4$ to be 5890 cm^{-1} (16.8 kcal mol^{-1}) and 4340 cm^{-1} (12.4 kcal mol^{-1}), respectively. The results may be compared with the values established by measuring the singlet–triplet energy differences in molecules of the $Mo_2Cl_4(PP)_2$ type,[7] namely, the δ-bond energy, 4840 cm^{-1} (13.8 kcal mol^{-1}), and the δ barrier, 3610 cm^{-1} (10.3 kcal mol^{-1}).

Singlet δ–δ* Transition

The dipole- and spin-allowed electronic transition between the ground state $^1\delta^2$ and the excited state $^1\delta\delta^*$ (the δ–δ* transition) may be the most extensively studied property of the δ manifold. Although the transition has been very well founded experimentally, almost all attempts to calculate the transition energy in compounds with the quadruple bonds have failed to provide acceptable results. The calculated transition energies appear to be at two extremes. The result given by the Xα method using a transition state approximation is always far lower than that observed due to a poor description of electron correlation in the ground state,[2] although improvement has been made by an Xα-VB method.[20] On the other hand, previous ab initio calculations including electron correlation[9,10] have predicted a transition energy that is much higher than that observed, as a result of failing to account for the so-called atomic intrapair correlation in the $^1\delta\delta^*$ state.[9]

Our present work is no exception. The δ–δ* transition energies from our present CASSCF calculations are all much higher than the measured results, at all values of the internal rotation angles as shown in Figure 7, where we show only the transition energies as χ changes from 90° to 45°, since the results in the region from 45° to 0° have, again, an approximate mirror symmetry. An important feature of Figure 7 is that the calculated results (the solid curve) are nearly parallel to those observed (the dashed curve showing the peaks of absorption), indicating a nearly constant error of the calculations that is independent of the angles of the internal rotation.

---

(20) Noodleman, L.; Norman, J. G., Jr. *J. Chem. Phys.* **1979**, *70*, 4903.

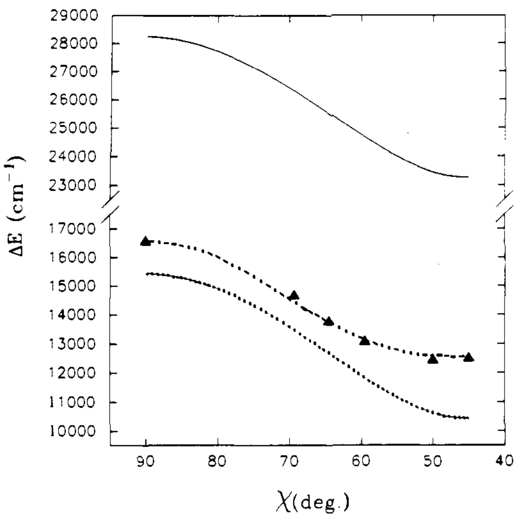

Figure 7. Comparison of the singlet δ–δ^* transition energies as a function of the internal rotation angles: (—) calculated results for $Mo_2Cl_4(PH_3)_4$; (---) from a non-linear least-square fitting of the measured results (▲) for molecules of the $Mo_2Cl_4(PP)_2$ type; (···) corrected results by subtracting 1.59 eV from the calculated results.

The nature of this error has been recognized by Hay[9] in his calculation of the same transition energy in $[Re_2Cl_8]^{2-}$ by the GVB method. It is well-known that, as in the valence-bond treatment, the $^1\delta\delta^*$ state can be shown by conventional LCAO MO theory to be a purely ionic state in which an atomic d orbital on one of the metal centers would be found to be doubly occupied. Very strong electron correlation is then associated with such a double occupation.[21] There is good reason[21,22] to expect that such an atomic intrapair correlation energy could be at least 1 eV in the second transition series. The CASSCF wave function employed in our present study is, however, not capable of treating this type of correlation properly, although it gives a good description of electron correlation in the ground state which is predominantly covalent. Absence of the atomic intrapair correlation energy in the $^1\delta\delta^*$ state in our calculations, therefore, leads to a high energy for the state.

There have been some attempts[23] to calculate the atomic intrapair correlation energy for pairs of 3d electrons. The correlation energy may also be estimated empirically or semiempirically as in an MGVB study on the Cr_2 and Mo_2 molecules by Goodgame and Goddard.[22] These authors corrected the correlation error that primarily arises from the negative ionic terms by decreasing the values of the one-center self-Coulomb integrals. The correction to the atomic self-Coulomb energy for a 4d pair in Mo atoms was given to be 1.59 eV. Simply accepting this value (1.59 eV) as the atomic intrapair correlation energy in our case may not be justified but, certainly, a good estimation of the correlation energy should not be very different from this value. As such, we then simply subtracted 1.59 eV from our calculated singlet δ–δ^* transition energies and plotted the results in Figure 7. As shown in the figure by the dotted curve, the final results have indeed improved dramatically and agree satisfactorily (ca. 1000 cm^{-1}) with the measured results.

Acknowledgment. We thank the National Science Foundation for support. We are grateful to Professor M. B. Hall and Dr. Z. Lin for helpful discussions and for access to their GAMESS program package. Texas A&M University Supercomputer Center is also thanked for granting computer time.

---

(21) Martin, R. L.; Hay, P. J. *J. Chem. Phys.* **1981**, *75*, 4539.

(22) Goodgame, M. M.; Goddard, W. A., III *Phys. Rev. Lett.* **1985**, *54*, 661.

(23) Jankowski, K.; Malinowski, P.; Polasik, M. *J. Phys. B* **1979**, *12*, 345 and references therein.

Solvent Effects. 4. Effect of Solvent on the *E*/*Z* Energy Difference for Methyl Formate and Methyl Acetate

Kenneth B. Wiberg* and Ming Wah Wong

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511.
Received July 9, 1992

Abstract: The effect of solvent on the difference in energy between the *E* and *Z* rotamers of methyl formate and methyl acetate has been studied using reaction field theory and the spherical cavity approximation. The calculated free energy difference for methyl formate was reduced from 5.2 kcal/mol in the gas phase to 1.6 kcal/mol for ϵ = 35.9 (acetonitrile). Similarly, with methyl acetate the difference was reduced from 8.5 to 5.2 kcal/mol. The changes in geometry, dipole moments, charge distributions, and vibrational frequencies on going from ϵ = 1 to 35.9 also were calculated and are in accord with increasing polar character of the carbonyl group in the more polar solvent. The change in *E*/*Z* energy difference for methyl formate was in very good agreement with that found previously using a more detailed treatment of the solvent interaction, and the change in energy difference for methyl acetate was also in good agreement with that calculated by statistical mechanics simulation. The change in equilibrium constant as a function of temperature in acetonitrile was calculated for methyl formate, and it was found that the change in dielectric constant of the solvent with temperature led to a much smaller than expected change in equilibrium constant with temperature. It is likely that the ΔH° and $\Delta H^\ddagger$ values derived by measuring equilibrium or rate constants as a function of temperature in polar solvents will often be considerably in error because of the change in solvent dielectric constant with temperature.

1. Introduction

The difference in properties between *Z*- and *E*-ester rotamers has been the subject of a number of experimental and theoretical studies. The *Z* rotamer of methyl formate has been found to be 4.8 kcal/mol more stable than the *E* form, and with methyl acetate the energy difference was found to increase to 8.5 ± 1 kcal/mol.[1] The barrier to rotation about the C–O bond for methyl acetate was 10–15 kcal/mol. The experimental results have been re-

---

(1) Blom, C. E.; Günthard, Hs. H. *Chem. Phys. Lett.* **1981**, *84*, 267.

0002-7863/93/1515-1078$04.00/0