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Substituted Oxirenes (X_2C_2O, X = BH_2, CH_3, NH_2, OH, F): Can They Be Made?

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Abstract: The oxirene system has received much attention recently; most theoretical studies have concentrated on the unsubstituted molecule while most experimentation has involved substituted oxirenes. In an effort to bridge the information gap between theory and experiment we have undertaken an *ab initio* study of substituted oxirenes. Predictions at various levels of theory up to the double-ζ plus polarization single and double coupled cluster with perturbative triples correction [DZP CCSD(T)] are presented for the series of substituted oxirenes with the formula X_2C_2O, where X = BH_2, CH_3, NH_2, OH, and F. Predictions from this level of theory are thought to be quite dependable on the basis of earlier work. Stationary points are compared among themselves and with the parent oxirene (X = H) and the molecular orbitals involved in ring bonding are analyzed, providing insight into the nature of the chemical bonding. Only the dimethyloxirene molecule (in addition to the earlier reported unsubstituted oxirene) is predicted to be a minimum on the DZP CCSD(T) surface. All other substituted oxirenes in the series are predicted to be transition states at that or lower levels of theory. Preliminary data from a benzooxirene study are also included.

Introduction

Three-membered rings, over the years, have received great attention in chemical research. From the unusually short bonds of cyclopropane to the enhanced stability of the cyclopropenyl cation, three-membered rings have been the fodder for multitudes of publications from both experimental and theoretical camps. The expanding body of evidence has provided a foundation for increasingly complex explanations that have improved our understanding of the nature of bonding. Of special interest in the case of three-membered rings are structure,[1] σ aromaticity,[2] π aromaticity and antiaromaticity,[3] ring-opening energetics,[4] and substituent effects.[5] To contribute to the understanding of the bonding involved in three-membered rings, we have undertaken an *ab initio* study of substituted oxirenes, performing a partial first-row scan of substituents. The molecules studied include oxirenes of the formula X_2C_2O, where X = BH_2, CH_3, NH_2, OH, and F. A preliminary examination of benzooxirene is also reported.

The homocycle hydrocarbon analogue of oxirene, cyclopropene, was the first three-membered ring involving a double bond to be synthesized.[6] Although this synthesis was reported in 1922, it was Schlatter's[7] synthesis in 1941 that brought this compound to more general notoriety. In 1959, Kasai, Myers, Eggers, and Wiberg[8] determined the structure of cyclopropene through microwave spectroscopy methods. A more accurate structural determination was performed by Stigliani, Laurie, and Li[9] in a 1975 microwave study. They, like Kasai *et al.*, observed the bond-length shortness characteristic of three-membered rings, but they especially noted that the double bond is significantly more short than is the single bond when compared to their typical counterparts.

Ab initio investigations of the C_3H_4 potential energy surface began as early as 1969[10] and have generally focused on the unimolecular reactions on the surface[11] (a topic reviewed by Steinmetz, Srinivasan, and Leigh[12]). The work of Kao and Radom[13] is one exception to this. They used the cyclopropene molecule as a model in the examination of molecular deformations. Amassing and examining the structural data of 34 derivatives of cyclopropene and the cyclopropenyl cation, Allen[14] found that π-acceptor substituents act to shorten vicinal bonds and lengthen distal bonds relative to analogous bonds in the unsubstituted species. Structural investigations of cyclopropene derivatives have not been overly abundant, but they do continue to appear.[15]

Although it has two electrons in a C–C π bond and two electrons in a C–H bonding orbital of the same symmetry, the cyclopropene molecule is not considered to meet the 4π requirements of "antiaromaticity". However, the heterocycles oxirene and thiirene, in which a chalcogen replaces the unique CH_2 unit of cyclopropene, *are* considered to be antiaromatic. Each chalcogen has a lone pair of the same symmetry (b_1) as the C–C π bond and, unlike the b_1 C–H bonding molecular orbital of cyclopropene, this lone pair is thought to more significantly interact with the π bond. Thus, with two electrons in the π bond and two electrons in the b_1 lone pair, oxirene and thiirene possess the 4 "π" electrons required for antiaromaticity.

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Certainly the late date of the first thiirene characterization (Krantz and Laureni, 1977[16]) compared to that of cyclopropene (1922[6]) implies a synthetic difficulty in thiirene due to destabilizing factors not present in the cyclopropene molecule. Additional evidence of such factors is provided by the relative lack of thermal stability.[16,17] Krantz and Laureni's matrix isolation report had some doubt cast upon it in 1978. Torres, Clement, Bertie, Gunning, and Strausz[17] noted that Krantz and Laureni observed too many peaks in the C–H stretching frequency region. In addition to their criticism, Torres *et al.* reported the preparation and identification of thiirene and several substituted thiirenes. Of these they noted that electron-withdrawing substituents substantially stabilize the system, with (carboethoxy)methylthiirene $[(H_3C)CSC(COOEt)]$ stable to at least 73 K.[17] In 1981 Krantz and Laureni produced additional details concerning the thiirene system and also observed IR bands for deuterated thiirene and methyl- and dimethylthiirene.[18]

As was the case for thiirene,[19] the first evidence for the transience of oxirene came from photochemical experiments implying a symmetric intermediate.[20] Unlike thiirene though, the parent C_2H_2O oxirene molecule has yet to be isolated. However, a few substituted oxirene compounds have been prepared. The first-reported *direct* evidence of an oxirene came in 1983 when Torres, Bourdelande, Clement, and Strausz[21] measured the IR spectrum of an unknown intermediate involved in the photolysis of hexafluoro-3-diazo-2-butanone. They assigned this spectrum to bis(trifluoromethyl)oxirene. This was contested by Langanis, Janik, Curphey, and Lemal,[22] but the original assignment was confirmed in 1987 when the problem was more comprehensively examined by Strausz and co-workers.[23] Meanwhile Debû *et al.* had reported the trapping of dimethyloxirene in rare gas matrices.[24] Since then, at least one other substituted oxirene has been detected[25] and two syntheses including a nominal oxirene ring have been reported,[26,27] both as part of rather large organic molecules. Both of the oxirenes in the syntheses differ from the previously mentioned oxirenes, as one carbon of the first[26] has two external bonds and the C═C bond of the second[27] is a part of a benzene ring.

Although the parent oxirene and its unimolecular potential energy surface have been repeatedly examined by theoretical methods,[28] the substituted oxirenes have, until now, remained nearly unscathed by the mark of theory. A recent submission from this group provides an up-to-date overview of the unsubstituted oxirene system and reports the characterization of the oxirene stationary point with a comprehensive list of available levels of theory.[29] The lack of theoretical data concerning substituent effects is rather surprising considering the significant substituent dependence of oxirene participation in the Wolff rearrangement as pointed out by Fenwick, Frater, Ogi, and Strausz[30] and the call-to-arms issued by Lewars in his 1983 review of oxirenes.[31] In the 1973 paper the importance of substituents on oxirene first could be grasped. By tabulating the percent oxirene participation in various Wolff rearrangements, Fenwick *et al.* demonstrated the fickleness of oxirenes. Its participation varied from 0 to 100% depending on the substituents and the experimental conditions. The dimethyloxirene participation was higher than that of any other system studied. Not surprisingly, dimethyloxirene was one of the first oxirenes to be isolated,[24] preceded only by the obviously similar system bis(trifluoromethyl)oxirene.[21] In their 1990 study employing both matrix-isolation and computational techniques Bachmann and co-workers[32] provided more evidence revealing the importance of substituents on oxirene. Because the experimental literature demonstrates the profound effect of substituents on oxirene and because of the severe want of theoretical inquiries into these effects, we have undertaken this study to help fill the void in understanding.

Theoretical Methods

This study was modeled after the earlier mentioned study of unsubstituted oxirene[29] and will mirror that study in many technical aspects. Four basis sets were used in the course of this investigation. The double-ζ plus polarization (DZP) basis set was constructed from the Huzinaga–Dunning[33] set of contracted Gaussian functions to which was added sets of six Cartesian d-type polarization functions on the heavy atoms[34] and a set of p-type polarization functions on the hydrogens.[35] The contraction scheme for this basis is as follows: B, C, N, O, F(9s5p1d/4s2p1d), H(4s1p/2s1p). The double-ζ plus polarization plus diffuse (DZP++) basis set was constructed by augmenting the DZP basis with diffuse s- and p-type functions on the heavy atoms[36] and a diffuse s-type function on each hydrogen.[37] The triple-ζ plus double polarization (TZ2P) basis set was formed by augmenting the Huzinaga–Dunning[38] triple-ζ basis with two sets of six Cartesian d-type functions on the heavy atoms[39] and two sets of p-type functions on the hydrogens.[40] The contraction scheme for this basis is as follows: B, C, N, O, F(10s6p2d/5s3p2d), H(5s2p/3s2p). The largest basis set used, [TZ2P(f,d)], is simply the TZ2P basis improved by the addition of ten Cartesian f-type functions on the heavy atoms[41] and six Cartesian d-type functions on the hydrogens.[42]

All structures were completely optimized within the given symmetry constraints using analytic gradient techniques. All four basis sets were utilized for self-consistent field (SCF) optimizations.[43] Only the DZP basis was used in conjunction with the single and double excitation configuration interaction (CISD),[44] singles and doubles coupled cluster

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(35) $\alpha_p(H) = 0.75$.

(36) $\alpha_s(B) = 0.0288$, $\alpha_p(B) = 0.0225$, $\alpha_s(C) = 0.0430$, $\alpha_p(C) = 0.0363$, $\alpha_s(O) = 0.0823$, $\alpha_p(O) = 0.0651$, $\alpha_s(F) = 0.1049$, $\alpha_p(F) = 0.0826$. Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 1784.

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(40) $\alpha_p(H) = 1.50$, $\alpha_p(H) = 0.375$.

(41) $\alpha_f(B) = 0.50$, $\alpha_f(C) = 0.80$, $\alpha_f(O) = 1.4$, $\alpha_f(F) = 1.85$.

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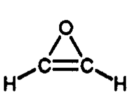
Table 1. Predicted Total Energies and Molecular Structures for the C_{2v}-Symmetry Structure of Oxirene[a,b]



level of theory	total energy	r(C—O)	r(C═C)	r(C—H)	∠CCH
DZP SCF	–151.617 18	1.466	1.251	1.066	162.6
DZP++ SCF	–151.621 89	1.464	1.251	1.066	162.7
TZ2P SCF	–151.642 83	1.465	1.240	1.059	162.2
TZ2P(f,d) SCF	–151.650 69	1.459	1.240	1.059	162.5
DZP CISD	–152.022 66	1.491	1.272	1.073	162.0
DZP CCSD	–152.073 17	1.506	1.285	1.078	161.8
DZP CCSD(T)	–152.090 85	1.515	1.292	1.080	161.7

[a] Energies in hartrees, bond lengths in angströms, bond angles in degrees. [b] All data in this table are taken from ref 29.

(CCSD),[45] and CCSD with perturbative triples correction [CCSD(T)][46] methods. At all correlated levels of theory, the five lowest-lying molecular orbitals were held doubly occupied (five frozen core), and the five highest virtuals were kept unoccupied (five frozen virtuals). The SCF force constants were determined via analytic second derivative procedures,[47] while all correlated force constants were determined by the method of finite differences. Most of this study was completed using the PSI program package,[48] while the TZ2P(f,d) SCF computations were handled with the CADPAC suite of programs.[49]

Results

To more conveniently compare the effects of substituents, an abbreviated table of the results from the earlier unsubstituted oxirene study[29] is included here. Table 1 gives total energies and geometrical parameters and Table 2 harmonic vibrational frequencies. Only the results from levels of theory equivalent to the levels used in this study are included; it should be noted that the earlier study, like this one, utilized frozen core in the correlated levels of theory, but unlike this study, no virtuals orbitals were held unoccupied (the geometrical and frequency changes due to this difference should be negligible). Two important trends in the predicted b_2 ring-deformation frequencies should be noted. The first is the basis set effect. With the SCF method, it is seen that, compared with the DZP basis set results, diffuse functions stabilize this frequency, the TZ2P basis destabilizes it, and the addition of higher-angular-momentum functions again stabilizes this mode. Not shown by Table 2 here, but demonstrated in detail by the earlier authors, is the fact that this trend continues at the correlated levels. Second, it is noted that as the treatment of electron correlation is improved this normal-vibrational mode is destabilized. These trends provide guidelines for the present study; first we establish the basis set trend with the SCF method and then correlation methods are applied to further characterize the stationary points. In light of the fact that with the SCF method the substituted oxirenes followed the same basis set trends as did the parent, only the DZP basis was used to further characterize the stationary points with the correlated methods. The similarity of trends to those seen in the earlier paper lends confidence to our current results although we have not exhausted all available theoretical tools, as did the previous study.

Diborooxirene. (a) Planar Structure. Tables 3 and 4 give the structural parameters and harmonic vibrational frequencies, respectively, for the planar C_{2v}-symmetry structure of diborooxirene. At all SCF levels of theory and at the DZP CISD level, this structure is a minimum. However, the b_2 ring-deformation mode becomes imaginary at the DZP CCSD level. Since the CCSD(T) method has been shown to destabilize this mode even more than CCSD for the parent molecule, no frequency determination was undertaken at the higher level of theory. We predict this C_{2v}-symmetry structure to be a transition state (the single imaginary mode corresponds to ring opening) rather than an intermediate.

Note that the trends in the b_2 ring-deformation frequency established in the unsubstituted oxirene for both basis set and electron correlation are followed here. Also of significant interest is the lengthening of the C═C bond and the shortening of the C—O bond relative to the unsubstituted oxirene caused by the BH_2 substituents. The highest level geometry determination [DZP CCSD(T)] shows a +0.035 Å change in the C═C bond length and a –0.034 Å change in the C—O bond length relative to the parent oxirene.

(b) Bisected Structure. The BH_2 substituent is one of the most interesting for quantum chemists as rotation by 90° "turns off" its π accepting capability. The C_{2v}-symmetry bisected structure with the BH_2 group rotated by 90° (perpindicular to the ring plane) is *not* a minimum at any level of theory. Each stationary point has two imaginary frequencies corresponding to BH_2 rotation. Only the DZP SCF and DZP CISD levels of theory were applied to this geometrical configuration (results shown in Table 5 and 6), as these levels provided sufficient data for exploring BH_2-substituent rotation.

There are a number of significant differences between this structure and the planar structure. The ring-deformation mode in the bisected structure is stabilized by 160 cm^{-1} at the DZP SCF level and an incredible 245 cm^{-1} at the DZP CISD level relative to the planar structure, due entirely to turning off the π acceptor. All three heavy atom bond lengths are also noticeably changed by the rotation of the BH_2 groups. The DZP CISD C—O bond length is 0.045 Å longer in the rotated structure, the C═C bond 0.023 Å shorter, and the C—B bond 0.012 Å longer. This bisected structure, when compared to its planar isomer, is 14.2 and 15.6 kcal/mol higher in energy at the DZP SCF and the DZP CISD level of theory, respectively.

Dimethyloxirene. On the dimethyloxirene potential energy surface only one minimum of C_{2v} symmetry was found at every level of theory employed. Tables 7 and 8 provide total energies, structural parameters, and harmonic vibrational frequencies.

The structural aspects of the dimethyloxirene ring are not very different from those of the parent oxirene. The C–O bond lengths of each are very similar with the dimethyloxirene having a slightly longer C–O bond (0.005 to 0.008 Å) than its unsubstituted counterpart at most levels of theory, although it is predicted to be 0.001 Å shorter at the DZP CISD level of theory. The C═C double bond length is very similar between the parent and dimethyl-substituted molecules, with the most significant difference coming at the DZP CISD level where the dimethyloxirene is predicted to have a C═C bond 0.006 Å shorter than the parent.

Several vibrational predictions are of particular interest. Starting with the mode which has received the most interest throughout this study and the earlier unsubstituted study,[29] we

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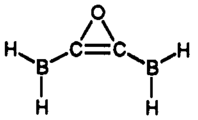
Table 2. Predicted Harmonic Vibrational Frequencies for the C_{2v}-Symmetry Structure of Oxirene[a,b]

level of theory	CH symm stretch (a_1)	C=C stretch (a_1)	CO symm stretch (a_1)	CH symm rock (a_1)	CH asymm wag (a_2)	CH symm wag (b_1)	CH asymm stretch (b_2)	CH asymm rock (b_2)	ring deform. (b_2)
DZP SCF	3581	1971	1170	994	786	673	3502	1087	445
DZP++ SCF	3584	1971	1171	995	789	675	3500	1087	457
TZ2P SCF	3575	1969	1160	982	785	677	3492	1094	416
TZ2P(f,d) SCF	3570	1975	1169	996	833	695	3488	1105	446
DZP CISD	3500	1866	1134	932	652	561	3427	1009	336
DZP CCSD	3429	1784	1099	890	552	487	3361	969	263
DZP CCSD(T)	3405	1739	1076	865	488	439	3339	947	119
DZP++ CCSD(T)	3410	1741	1074	865	489	464	3336	945	165
TZ2P CCSD(T)	3392	1739	1055	846	476	418	3314	936	85 *i*
TZ2P++ CCSD(T)	3391	1738	1053	846			3313	937	13 *i*
TZ2P(f,d) CCSD(T)	3407	1763	1067	873	591	514	3338	960	163

[a] Harmonic vibrational frequencies in cm^{-1}. [b] All data in this table are taken from ref 29.

Table 3. Predicted Total Energies and Molecular Structures for the C_{2v}-Symmetry Planar Structure of Diborooxirene[a]



level of theory	total energy	r(C—O)	r(C=C)	r(C—B)	∠CCB
DZP SCF	−202.163 05	1.450	1.277	1.545	158.9
DZP++ SCF	−202.168 66	1.449	1.277	1.544	159.2
TZ2P SCF	−202.194 26	1.449	1.267	1.539	158.3
TZ2P(f,d) SCF	−202.203 54	1.444	1.267	1.538	158.4
DZP CISD	−202.694 68	1.465	1.297	1.536	158.2
DZP CCSD	−202.792 25	1.478	1.315	1.538	158.0
DZP CCSD(T)	−202.818 07	1.481	1.327	1.537	157.9

[a] Energies in hartrees, bond lengths in angströms, bond angles in degrees.

note that at all SCF levels of theory the dimethyloxirene b_2 ring-deformation frequency is lower than the frequency of that same mode in the parent. It is seen, however, that electron correlation affects the unsubstituted oxirene deformation mode more than it does the dimethyloxirene deformation mode. In the case of the parent molecule, the correlation effects on the frequency of the b_2 ring-deformation mode are the following: DZP SCF to DZP CISD, −109 cm^{-1}; DZP CISD to DZP CCSD, −73 cm^{-1}; DZP CCSD to DZP CCSD(T), −144 cm^{-1}. In the dimethyloxirene case, these are reduced to −40, −77, and −109 cm^{-1}, respectively, so that at the highest level of theory [DZP CCSD(T)] the dimethyloxirene ring-deformation mode is predicted to have a higher frequency than that mode in the parent oxirene itself. Since the stabilization offered by the TZ2P(f,d) basis set with the SCF method is seen to be greater for dimethyloxirene than for the parent and since the earlier study[29] showed the TZ2P(f,d) CCSD(T) ring-deformation frequency to be 44 cm^{-1} higher than the DZP CCSD(T) value, it is with confidence that we predict the dimethyloxirene stationary point to be a true minimum on the potential energy surface.

Two further frequency comparisons ought to be made here. First, we point out that while frequency of the b_2 ring-deformation mode is similar to and (at the highest level of theory) larger than that frequency in the parent, the C–O symmetric frequency is consistently and substantially lower. At the DZP CCSD level of theory, the dimethyloxirene a_1 C–O stretching frequency is 182 cm^{-1} lower than that of the unsubstituted oxirene.

Additionally, the stretching frequency of the C=C double bond should be mentioned. The experimentally observed 2137 cm^{-1} band had been assigned to ν(C=C)[24] and defended through the use of the 3-21G SCF *ab initio* method which predicted a value of 2242 cm^{-1} for this mode.[32] Their assigned frequency is abnormally large for a C=C stretching frequency, but our predictions agree that this mode should have an elevated frequency. The highest level of theory applied to this frequency determination (DZP CCSD) predicts a value of 2102 cm^{-1}. On the basis of the unsubstituted oxirene study,[28] we expect the CCSD(T) results to be lower for this frequency but the TZ2P-(f,d) basis set results to be higher. These effects are not predictable in a quantitative manner nor are the matrix effects on the observed frequency, but these effects should not change the frequency by more than 100 cm^{-1}. Thus our predictions are in the ballpark of the fundamental assignment of Debû *et al.*[24] This C=C stretching frequency is dramatically increased from the unsubstituted oxirene to the dimethyloxirene. With all levels of theory this increase is quite profound. Comparison at the DZP CCSD level of theory shows the dimethyloxirene C=C stretching frequency to be 318 cm^{-1} higher than the C=C stretching frequency of the parent molecule.

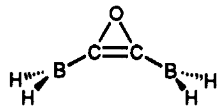
Diaminooxirene. No minimum was found for this molecule which corresponded to an oxirene. The only C_{2v}-symmetry stationary point which was located had three imaginary vibrational frequencies: one corresponding to b_2 ring deformation and two corresponding to NH_2 rotation. Following these two rotation modes leads to two additional stationary points, one of C_s symmetry and another of C_2 symmetry. Frequency analyses of these stationary points show them both to be transition states. The single imaginary frequency in each case corresponds to asymmetric ring deformation (which should lead to the ketene) and is larger in magnitude than the analogous imaginary ring-deformation frequency predicted for the C_{2v}-symmetry stationary point. At this low level of theory (DZP SCF) the C_2-symmetry and C_s-symmetry stationary points lie 3.4 and 3.5 kcal/mol below the C_{2v}-symmetry structure.

Table 4. Predicted Harmonic Vibrational Frequencies for the C_{2v}-Symmetry Planar Structure of Diborooxirene[a]

level of theory	C=C stretch (a_1)	CO symm stretch (a_1)	CB symm stretch (a_1)	CB symm rock (a_1)	CB asymm wag (a_2)	CB symm wag (b_1)	CB asymm stretch (b_2)	CB asymm rock (b_2)	ring deform. (b_2)
DZP SCF	2127	1130	749	195	432	105	937	385	288
DZP++ SCF	2128	1125	746	195	447	122	929	380	295
TZ2P SCF	2120	1100	739	192	389	85	915	376	248
TZ2P(f,d) SCF	2127	1121	740	175	414	135	952	421	307
DZP CISD	2041	1110	746	190	420	90	1010	367	135
DZP CCSD	1942	1070	731	186			1001	354	152i

[a] Harmonic vibrational frequencies in cm^{-1}.

Table 5. Predicted Total Energies and Molecular Structures for the C_{2v}-Symmetry Bisected Structure of Diborooxirene[a]



level of theory	total energy	r(C—O)	r(C═C)	r(C—B)	∠CCB
DZP SCF	−202.140 36	1.488	1.257	1.558	169.9
DZP CISD	−202.669 87	1.510	1.274	1.548	171.3

[a] Energies in hartrees, bond lengths in angströms, bond angles in degrees.

Dihydroxyoxirene. As was the case for diaminooxirene, no minimum with equivalent C–O bonds was located. Two planar structures (*cis* and *trans*, where these terms refer to the relationship of the hydrogen to the oxygen of the ring) of C_{2v} symmetry were located, but each of these has two imaginary frequencies corresponding to C–C–O–H torsion. When the symmetry constraint is reduced from C_{2v} to C_2 and C_s and these torsion modes are followed, two additional structures are located. The same lower-symmetry structures are located whether starting from the *cis* or *trans* isomer. However, whereas the ring-deformation mode has positive curvature in the C_{2v}-symmetry structures, it has negative curvature in each of the lower-symmetry structures. Thus, each of the lower-symmetry structures are transition states with the one imaginary frequency corresponding to ring opening. The *trans* structure is 4.8 kcal/mol higher in energy than the *cis* structure, while the C_s-symmetry and C_2-symmetry structures are 2.3 and 2.7 kcal/mol lower in energy than the *cis* isomer.

Since no diamino- or dihydroxyoxirene minimum exists on the DZP SCF potential energy surface, no further investigation of these molecules was undertaken and discussion concerning them will, henceforth, be extremely limited.

Difluorooxirene. Completing the first-row sweep of oxirene systems with the formula X_2C_2O is difluorooxirene. Tables 9 and 10 provide data concerning the structure and harmonic vibrational frequencies for the C_{2v}-symmetry stationary points. One C_{2v}-symmetry stationary point was found for this oxirene at each level of theory applied. All levels of theory predict the C_{2v}-symmetry structure to be a minimum except the highest one applied here. The DZP CCSD(T) method predicts this structure to be a transition state. The ring-deformation mode becomes imaginary with the inclusion of the triples correction. In the case of the unsubstituted oxirene it it seen that the TZ2P(f,d) basis provides 44 cm^{-1} stabilization to this mode with the CCSD(T) method. Thus, as the imaginary frequency of difluorooxirene is of very low magnitude, we are unable to predict with absolute certainty whether the difluorooxirene species is a transition state rather than an intermediate. However, if higher levels of theory would predict difluorooxirene to be a true minimum, then the ring-deformation mode would certainly have an extremely low frequency.

The fluorine substituents do shorten the ring bond lengths, the C═C double bond more profoundly than the C—O bond. The C—O bond is 0.004 Å shorter in the F_2C_2O structure than in the H_2C_2O structure and the C═C bond is 0.015 Å shorter at the DZP CCSD(T) level. At all levels of theory we predict the ring-deformation frequency to be below that of the parent oxirene, though part of this difference is due to the additional mass of fluorine. The facts that all predicted ring-deformation frequencies are lower than those of the unsubstituted oxirene and that difluorooxirene follows the same trends as oxirene itself are consistent with the highest-level predictions that difluorooxirene is a transition state and show that fluorines are destabilizing to the oxirene ring even though they are electron withdrawing.

Benzooxirene. We report here a preliminary benzooxirene investigation, undertaken primarily to satisfy the authors' curiosity. At this point in the study, we have examined only the planar C_{2v}-symmetry structure of benzooxirene. This structure happens to be a minimum at the SCF level of theory. However, based upon the work of Hehre and Pople,[50] as well as Wagner and co-workers,[51] on other two-ring systems and Lewars'[52] unpublished study of this system at correlated levels of theory, it is suspected that the true structure is nonplanar. Figure 1 depicts the geometry predicted by the TZ2P(f,d) SCF level of theory. Of interest concerning this stationary point are the C—C bond lengths in the benzene ring and the comparatively large oxirene ring-deformation frequency. The bond lengths show the ring tending toward a structure with bonds more localized than is usual for substituted benzenes. The large oxirene ring-deformation frequency (479 cm^{-1} at the TZ2P(f,d) SCF level of theory) indicates that benzooxirene and its derivatives may be more synthetically feasible than the other substituted oxirenes (see also ref 27). It is obvious from our initial glance at this system that aromatic (or antiaromatic) ring substitutions onto oxirene deserve a fully study unto themselves. Additional information is available from the authors upon request and it is our hope that this initial report might spark additional studies of this and other double-ring oxirene systems.

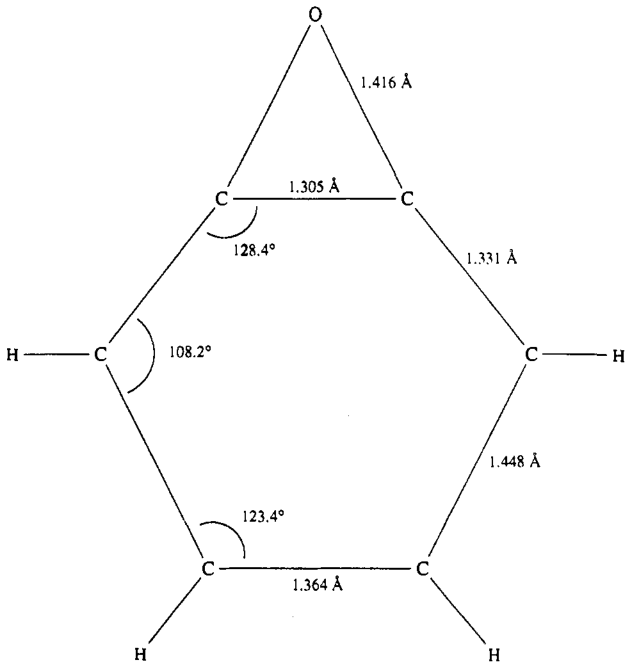


Figure 1. Benzooxirene geometrical parameters at the TZ2P(f,d) SCF level of theory.

Discussion

Periodic Comparison. Table 11 reports the C—O bond distances and harmonic vibrational frequencies of all stationary points investigated at various levels of theory. It can be seen that the substituted oxirenes to the degree at which they are studied here follow the same trends with regards to basis set and increased correlation as does the unsubstituted oxirene. Another trend that ought to be noted is as follows: comparison of C–O bond lengths and the frequency of the associated ring-deformation mode reveals that the stationary points with longer C–O bonds generally have higher ring-deformation frequencies. The stationary points with shorter bonds to generally have higher a_1 C–O stretching frequencies, but the trend in b_2 ring-deformation

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(50) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.

(51) Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210.

(52) Personal communication 1994, MBPT2 level of theory.

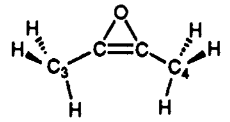
(53) Xie, Y.; Tian, A.; Yan, G. *J. Sichuan Univ., Natl. Sci. Ed.* **1986**, *3*, 124.

Table 6. Predicted Harmonic Vibrational Frequencies for the C_{2v}-Symmetry Bisected Structure of Diborooxirene[a]

level of theory	C═C stretch (a_1)	CO symm stretch (a_1)	CB symm stretch (a_1)	CB symm rock (a_1)	CB asymm wag (a_2)	CB symm wag (b_1)	CB asymm stretch (b_2)	CB asymm rock (b_2)	ring deform. (b_2)
DZP SCF	2205	970	712	157	369	167	1123	287	448
DZP CISD	2118	948	706	139	316	152	1114	238	380

[a] Harmonic vibrational frequencies in cm^{-1}.

Table 7. Predicted Total Energies and Molecular Structures for the C_{2v}-Symmetry Structure of Dimethyloxirene[a]



level of theory	total energy	r(C—O)	r(C═C)	r(C_1—C_3)	∠$C_2C_1C_3$
DZP SCF	–229.733 30	1.474	1.251	1.474	164.8
DZP++ SCF	–229.738 83	1.470	1.252	1.473	165.0
TZ2P SCF	–229.769 00	1.472	1.242	1.465	164.5
TZ2P(f,d) SCF	–229.778 58	1.466	1.242	1.463	164.6
DZP CISD	–230.366 61	1.490	1.266	1.471	164.5
DZP CCSD	–230.495 77	1.511	1.283	1.478	164.2
DZPCCSD(T)	–230.523 24	1.520	1.290	1.480	164.2

[a] Energies in hartrees, bond lengths in angstrõms, bond angles in degrees.

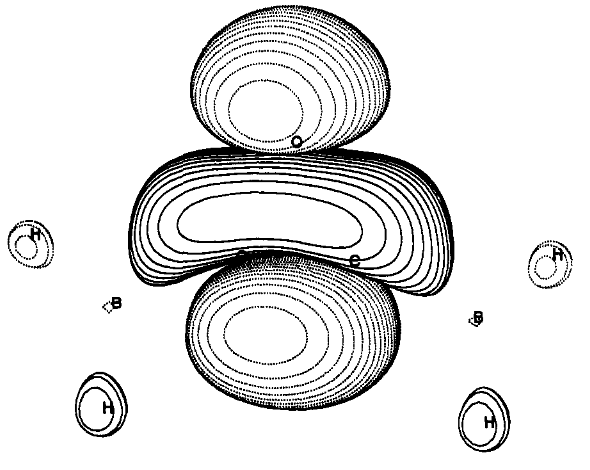


Figure 2. The $9a_1$ orbital of planar diborooxirene.

frequencies is a significant exception to the general rule that shorter bonds have higher stretching frequencies. It must be remembered, though, that the b_2 ring-deformation mode, although it is a mode involving C–O stretching, does not so much reflect the strength of the C–O bond as it does the tendency toward ring opening and can be considered a bond angle coordinate. Thus it makes sense that the stationary points with shorter C–O bonds would have smaller ring-deformation frequencies. The more compact the "4π antiaromatic" system is, the more favorable is the breaking of its high-energy ring.

Molecular Orbital Observations. It has been remarked that since electron-withdrawing substituents stabilized thiirene, such substituents might also stabilize oxirene.[23] We have found in this study that it is not so much *that* electrons are withdrawn but rather *how* these electrons are withdrawn that stabilizes the oxirene ring. The fluorine atom as a substituent destabilizes the oxirene ring while methyl groups stabilize the ring. Surely then the cause for thiirene and oxirene stabilization must be due to a more complex interaction between substituent and ring. The capacity to illuminate such daedalian labyrinths through the computation of molecular orbitals is one of the strengths of *ab initio* methods.

Our discussion of molecular orbitals will be held to configuration interaction natural orbitals computed at the DZP CISD level of theory. We shall start with an examination of the two diborooxirene stationary points and then extend the arguments developed in understanding the ring stabilization and destabilization of these to the dimethyl and difluoro systems. As mentioned earlier, the BH_2 substituent is one of great interest to quantum chemists because of its theoretically rotatable empty p orbital. In the lower-energy diborooxirene planar structure, the empty p orbitals of the BH_2 groups are oriented out of plane and thus conjugate with the oxirene π system. This conjugation does not, however, stabilize oxirene as a ring system. The C═C bond is lengthened as π density is shared with the BH_2 groups and the C—O bond lengths are shortened, but the b_2 ring-deformation mode decreases in frequency. This demonstrates that while the π system does become more delocalized and the C—O bond does become stronger, this does not necessarily mean that the structure will be stabilized as a *ring*; in fact it is destabilized with regards to ring opening.

When the BH_2 groups are rotated we note a significant increase in energy (15.6 kcal/mol at the DZP CISD level) and numerous other changes: the C—O bond lengthens, the C—B bond lengthens, the C═C bond shrinks, and the b_2 ring-deformation frequency substantially increases. The C—B and C═C bond length changes are relatively simple to understand as in the bisected structure the empty p orbitals of BH_2 no longer conjugate with the π system of the ring. So, as the system is destabilized, why is there an increase in the frequency of the ring-deformation mode? The answer lies in the molecular orbitals, and in simple terms it is due to the participation of the empty p orbitals of the BH_2 groups in the ring-bonding orbitals.

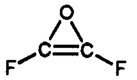
A side-by-side comparison of the doubly occupied orbitals of the two diborooxirene stationary points (requiring far too many figures for this report—our discussion will stick to the most salient features) reveals several reasons for the ring stabilization of the bisected structure. The $7a_1$ molecular orbital of the planar structure is mostly BH_2 bonding, but it is seen to be spread across the entire molecule. The ring portion of this molecular orbital is antibonding between the carbons and the oxygen. When the BH_2 groups are rotated this orbital becomes a b_2 molecular orbital with essentially no contribution from the carbons of the ring. The highest doubly occupied orbitals of a_1 symmetry ($9a_1$ for the

Table 8. Predicted Harmonic Vibrational Frequencies for the C_{2v}-Symmetry Structure of Dimethyloxirene[a]

level of theory	C═C stretch (a_1)	CO symm stretch (a_1)	CC_{met} symm stretch (a_1)	CC_{met} symm rock (a_1)	CC_{met} asymm wag (a_2)	CC_{met} symm wag (b_1)	CC_{met} asymm stretch (b_2)	CC_{met} asymm rock (b_2)	ring deform. (b_2)
DZP SCF	2280	990	749	230	416	164	1229	436	362
DZP++ SCF	2276	991	749	232	427	168	1229	448	373
TZ2P SCF	2267	974	744	232	436	173	1222	441	346
TZ2P(f,d) SCF	2277	990	750	236	451	176	1225	454	389
DZP CISD	2204	964	741	221	367	153	1213	399	322
DZP CCSD	2102	917	717	211			1179	370	245
DZP CCSD(T)							1166	357	136

[a] Harmonic vibrational frequencies in cm^{-1}.

Table 9. Predicted Total Energies and Molecular Structures for the C_{2v}-Symmetry Structure of Difluorooxirene[a]



level of theory	total energy	r(C—O)	r(C═C)	r(C—F)	∠CCF
DZP SCF	−349.341 10	1.457	1.233	1.269	163.0
DZP++ SCF	−349.347 17	1.454	1.235	1.268	163.3
TZ2P SCF	−349.390 96	1.455	1.227	1.263	163.1
TZ2P(f,d) SCF	−349.406 33	1.450	1.227	1.260	163.4
DZP CISD	−350.002 03	1.478	1.251	1.282	162.5
DZP CCSD	−350.117 41	1.500	1.269	1.295	161.9
DZP CCSD(T)	−350.144 00	1.511	1.277	1.298	161.8

[a] Energies in hartrees, bond lengths in angströms, bond angles in degrees.

planar and $8a_1$ for the bisected configuration) involve in-plane ring bonding through the use of carbon and oxygen p orbitals and are more delocalized over the entire molecule in the bisected case where the empty p orbitals of the BH_2 groups can also contribute (see Figures 2 and 3). The b_2 molecular orbitals of the two structures are rather similar although it should be kept in mind that the $4b_2$ B–H bonding molecular orbital of the planar structure rotates to an a_2 molecular orbital in the bisected structure; in neither case does it participate in the ring bonding.

In consideration of the out-of-plane orbitals we note that in the parent oxirene, the hydrogens are unable to participate in the π system of the ring because they possess no occupied or low-lying p orbitals. All substituents in this study, however, are capable of participating in molecular orbitals that have a nodal plane coplanar with the ring. In the out-of-plane b_1 orbitals we find another difference between the planar and bisected forms of diborooxirene. The planar structure has two doubly occupied b_1 molecular orbitals whereas the bisected structure has three. While it was expected that the planar structure's empty BH_2 p orbitals would spread the "4π antiaromatic" electrons, it is seen that their participation is limited to the C═C portion; the $1b_1$ molecular orbital (Figure 4) has no appreciable participation from the borons and the $2b_1$ orbital (Figure 5) has a node between the carbons and the oxygen and significant boron–carbon bonding overlap. The $1b_1$ orbital of the bisected structure (Figure 6), on the other hand, has no nodes and some bonding participation from the borons and hydrogens. The $2b_1$ orbital is mostly B–H bonding (as mentioned above) with a node between the borons and the oxygen approximately at the position of the carbons, and the $3b_1$

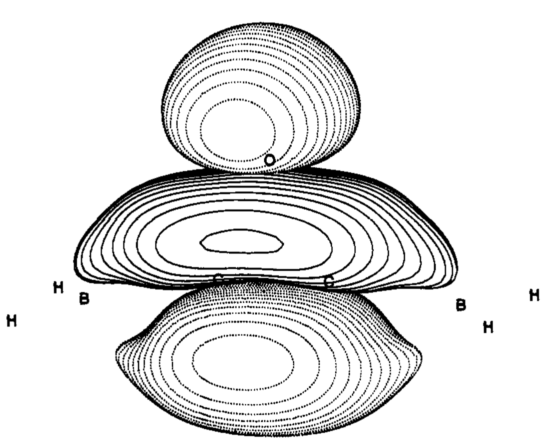


Figure 3. The $8a_1$ orbital of bisected diborooxirene.

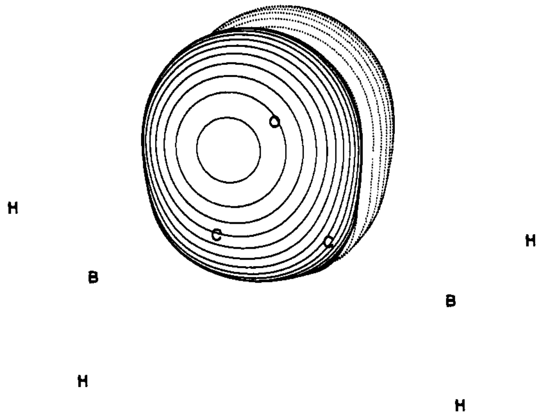


Figure 4. The $1b_1$ orbital of planar diborooxirene.

Table 10. Predicted Harmonic Vibrational Frequencies for the C_{2v}-Symmetry Structure of Difluorooxirene[a]

level of theory	CC stretch (a_1)	CO symm stretch (a_1)	CF symm stretch (a_1)	CF symm rock (a_1)	CF asymm wag (a_2)	CF symm wag (b_1)	CF asymm stretch (b_2)	CF asymm rock (b_2)	ring deform. (b_2)
DZP SCF	2482	1248	865	334	480	266	1479	649	305
DZP++ SCF	2473	1249	862	334	462	257	1477	643	313
TZ2P SCF	2439	1218	857	336	500	268	1449	648	269
TZ2P(f,d) SCF	2458	1233	863	339	524	277	1466	656	296
DZP CISD	2374	1208	827	315	383	218	1415	608	242
DZP CCSD	2253	1142	781	295	238	157	1347	570	159
DZP CCSD(T)	2200	1105	764	287	115	116	1321	549	78i

[a] Harmonic vibrational frequencies in cm^{-1}.

Table 11. Comparison of Substituted Oxirenes[a]

	DZP SCF		TZ2P(f,d) SCF		DZP CISD		DZP CCSD(T)	
	r(C—O)	ring deform.	r(C—O)	ring deform.	r(C—O)	ring deform.	r(C—O)	ring deform.
–H	1.466	445	1.459	446	1.491	336	1.515	119
–BH_2: planar	1.450	288			1.465	135		
bisected[b]	1.488	448			1.510	380		
–CH_3	1.474	362	1.466	389	1.490	322	1.520	136
–NH_2: C_{2v}[b]	1.474	67i						
C_2	1.467	286i						
C_s	1.465	302i						
–OH: C_{2v} *trans*[b]	1.456	373						
C_{2v} *cis*[b]	1.475	318						
C_s	1.472	272i						
C_2	1.472	214i						
–F	1.457	305	1.450	296	1.478	242	1.511	78i

[a] Bond lengths in angströms, harmonic vibrational frequencies in cm^{-1}. [b] These stationary points have, in addition to any imaginary frequencies given here, two imaginary frequencies corresponding to XH_n rotation.

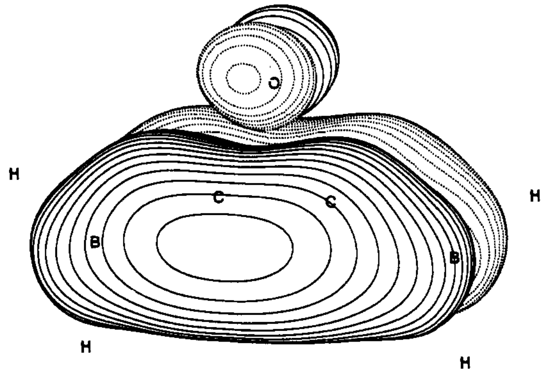


Figure 5. The $2b_1$ orbital of planar diborooxirene.

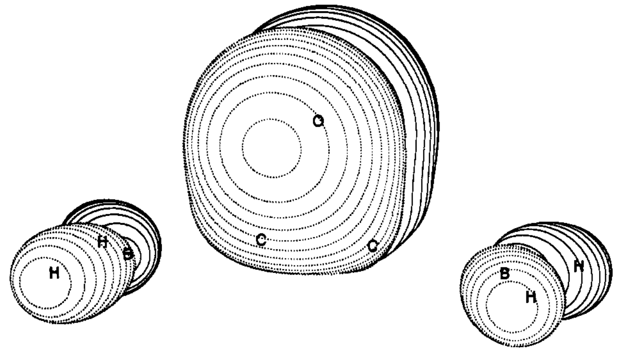


Figure 6. The $1b_1$ orbital of bisected diborooxirene.

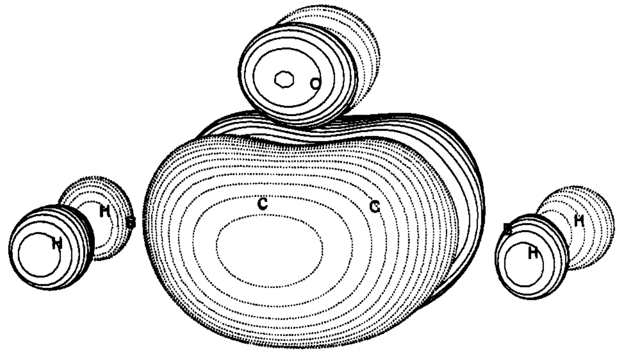


Figure 7. The $3b_1$ orbital of bisected diborooxirene.

orbital (Figure 7) is mostly C═C π bonding with some carbon–oxygen antibonding and nodes at the positions of the boron atoms. Thus we note that the bisected structure is actually more effective in dispersing the out-of-plane electron density than is the planar configuration.

We have remarked that the bisected structure provides a more beneficial spreading of in-plane and out-of-plane interactions with the oxirene *ring* system than does its planar counterpart. The empty p orbitals of the BH_2 groups conjugate with the C═C π bond when in the preferred planar conformation but with the oxirene ring when in the bisected conformation. The planar structure experiences much interaction between the carbons and borons but little boron interaction with the ring bonding. The bisected structure more effectively spreads the electrons of the oxirene ring. It is precisely these electron–spreading interactions that stabilize the ring-deformation mode in the bisected form. The planar structure provides more stabilization to the *system*, but the bisected structure provides more stabilization to the *ring*.

With this information in mind, we move on to examination of dimethyloxirene. It is known that methyl groups act as π acceptors. This is often explained in terms of hyperconjugation. The π*-like combination of C–H antibonding orbitals is theorized to conjugate with π systems. Hyperconjugation has been used to explain many geometrical and conformational observations.

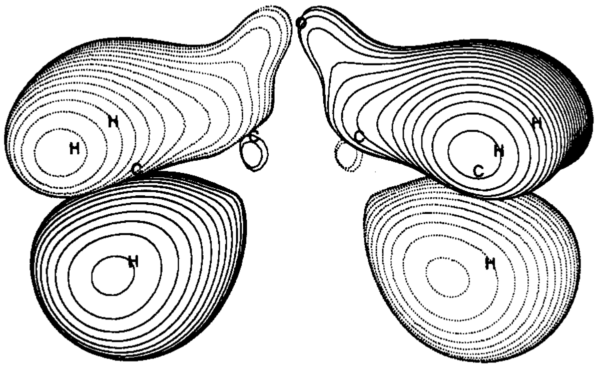


Figure 8. The $4b_2$ orbital of dimethyloxirene.

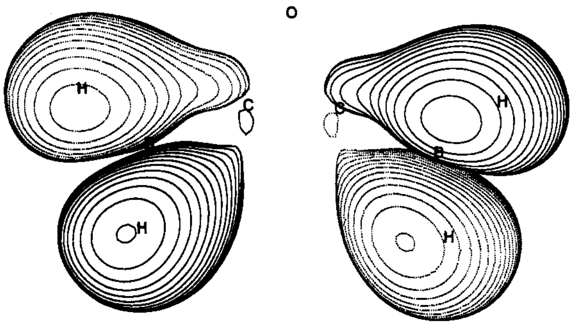


Figure 9. The $4b_2$ orbital of planar diborooxirene.

In a very simplistic view, the methyl group can be thought to accept electron density into the gap between hydrogens, similar to the way BH_2 groups accept electron density into their empty p orbitals.

Examination of the dimethyloxirene geometry (pictured above Table 7) reveals that a gap between methyl hydrogens is lined up with the C–O bond of the ring. When viewed in comparison to the diborooxirene stationary points, this conformation is more like the bisected structure than the planar one; the electron-accepting orbital is aligned to stabilize the ring. The in-plane and out-of-plane orbitals of dimethyloxirene are very similar to those of the bisected diborooxirene structure, but the four additional electrons of dimethyloxirene are in molecular orbitals similar to the $7a_1$ and $4b_2$ orbitals of the planar diborooxirene (the orbitals that become $1a_2$ and $2b_1$ upon rotation of the BH_2 groups). One important difference should be noted though: the $4b_2$ molecular orbital of dimethyloxirene (Figure 8) has appreciable bonding overlap with the oxygen whereas the $4b_2$ molecular orbital of the planar diborooxirene (Figure 9) has none whatsoever. This overlap provides additional stabilization to the oxirene ring.

We have seen thus far that properly directed π acceptance stabilizes the oxirene ring, but what of the interaction of the fluorine p orbitals with the oxirene ring orbitals? The difluorooxirene molecular orbitals are very different from those already discussed. The fluorine p orbitals, less diffuse and lower in energy than those of boron and carbon, seldom interact with the ring as a whole. Instead the fluorine orbitals are used solely for C–F bonding and fluorine core and lone pairs. The one exception to this is the $1b_1$ difluorooxirene molecular orbital. This molecular orbital is made up mostly of out-of-plane fluorine lone pairs, but some positive overlap with the oxirene ring, especially the oxygen of the ring, is present. The fact that fluorine is stingy with its p orbitals prevents the difluorooxirene ring from being stabilized to the degree that the dimethyloxirene ring is stabilized.

Conclusions

Of all the oxirenes with the formula X_2C_2O, where X = BH_2, CH_3, NH_2, OH, F, we predict that only one, dimethyloxirene, will be a true minimum on the potential energy surface. Both the diamino- and the dihydroxyoxirenes are predicted by SCF theory to be transition states, whereas the diborooxirene is predicted by SCF and CISD theories to be a minimum, but a transition state at the DZP CCSD level, and difluorooxirene is predicted to be a minimum at all levels of theory applied except the highest [DZP CCSD(T)] which predicts it to be a transition state. In all these transition state cases, stationary points with a single imaginary frequency corresponding to the asymmetric ring-deformation normal mode of vibration were located and characterized.

Our predictions concerning the dimethyloxirene minimum hold well with experimental observations. The observed v(C═C)[24] of unusually high frequency is plausibly reproduced. The fact that at the highest level of theory the ring-deformation mode of dimethyloxirene has a higher frequency than that of the unsubstituted oxirene also sits well with the fact that dimethyloxirene has been more experimentally accessible than the parent.[24,32] Additionally, dimethyloxirene should be easier than unsubstituted oxirene to observe because hydrogen migration is much more facile than methyl migration. The additional stability of dimethyloxirene has been explained through the examination of molecular orbitals and can be viewed as being due to hyperconjugation between the C–O bond and the methyl substituents.

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