various methods for averaging of individual methyl group rotation within the *tert*-butyl group may also be devised. However, such schemes can be expected to yield results that will qualitatively parallel the ones presented here.

A search for a unique metal position was carried out for all of the data presented in Table II employing combinations of the methods of averaging. This search was made with the lanthanide–oxygen bond oriented in the plane of the two lone pairs of electrons as shown in Figure 1, at angles of between 0 and ±55° to the carbonyl-bond axis. In general no such unique position could be found, which would simultaneously conform to both the shift and the relaxation data. The behavior of the praseodymium complex is typical. Using the RR method of averaging for both groups, a fit for the shift data was found at a distance of 2.1 Å at 15° toward the methyl group. For this position, the calculated relaxation data fits to within ±10% of the observed values. The relaxation data gave a position with a distance of 3.1 Å at an angle of 20° toward the methyl group. For this position, there was now a 10% discrepancy between the calculated and observed shift values. The only exception to this trend was observed for the ytterbium complex in conjunction with the application of the FR method of averaging for both groups. In this particular case an Yb–O distance of 4 Å was obtained, oriented at 18° toward the methyl group. Good fits of shift data for oxygen-containing substrates with LSR's have been reported.[2] For unsymmetrical ketones,[9,10] these fits are for unique positions which resemble the one obtained now for praseodymium. However, it is clear from the above discussion that these unique positions may in fact be fictitious. We suggest that a more rigorous way of arriving at LSR–substrate geometries is by the simultaneous fitting of both shift and relaxation data along the lines presented here.

Conclusions

The multisite approach should be applied in analyzing LSR data for substrates containing atoms with more than one lone pair of electrons; e.g., the carbonyl group should be treated as having two sites for LSR coordination. The population in each site is sensitive to steric effects of the substituents. In simulation of the shift or relaxation data from LSR experiments, appropriate rotational averaging must be carried out for substrates where rotation can occur. The simultaneous application of both shift and relaxation rate data to derive information concerning the LSR–substrate complex removes many of the ambiguities present if only one kind of data is employed.

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(19) The relaxation rate due to dipolar interaction is normally given by the square of local field components modulated by reorientation processes with a correlation time τ_c. The local field is proportional to $1/r^3$. If r can assume a range of values an average has to be taken. The average of $1/r^3$ has to be taken when the averaging process is fast compared to τ_c, since an average local field is established before reorientation has taken place. If the averaging process is slower than τ_c, the average of $1/r^6$ has to be computed since in this case relaxation occurs at different local fields. In choosing to calculate $[1/r^3]_{av}{}^2$ we have assumed that internal rotation is the fastest process.

(20) Note that for eq 5 or 6 to be valid the mean residence time at each site has to be short compared to the reciprocal of the chemical shift or of the line-width differences between the two sites.

Conformational Studies of 1,3-Dienes

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Abstract: The relative energies of trans, cis, and gauche conformers of butadiene, glyoxal, and acrolein and their fluoro-, chloro-, and cyano-substituted derivatives have been investigated using single determinant ab initio molecular orbital theory. In all cases the s-trans conformer was found to be the most stable form. The second stable isomer is either s-cis (acrolein and its derivatives, glyoxal itself) or gauche (substituted glyoxals, butadiene, and substituted butadienes). The fluctuations of the cis-trans energy difference and the tendency of the cis form to distort away from planarity are rationalized by perturbationally building up the π-orbital manifold of the various molecules from the π MO's of their constituent fragments.

The most stable conformer of butadiene,[2] acrolein,[3] and glyoxal[4] is planar s-trans. With a few exceptions[5] this rule also holds for the mono- and disubstituted parents of these three basic dienes.[6-8] The second stable conformer, when sufficiently close above the trans form so as to make its experimental detection possible, appears to s-cis,[4,7b,d-g] s-cis or gauche,[2f,7g,h] or gauche.[2f,8a-d] Three questions therefore arise: Are electronic effects responsible for the s-trans form being generally the most

Table I. Theoretical Energies for 1,3-Butadiene, Glyoxal, and Acrolein (hartrees)

Molecule	STO-3G Cis	STO-3G Trans	4-31G Cis	4-31G Trans
1,3-Butadiene	−153.017 42	−153.020 29	−154.693 85	−154.699 29
Glyoxal	−223.578 95	−223.581 43	−226.233 43	−226.242 05
Acrolein	−188.302 19	−188.302 84	−190.476 53	−190.477 84

Table II. Theoretical (STO-3G) Energies for Substituted 1,3-Butadiene, Glyoxal, and Acrolein (hartrees)

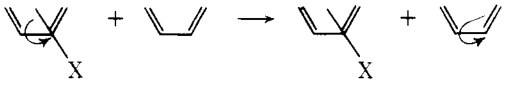
Molecule	X = F Cis	X = F Trans	X = Cl Cis	X = Cl Trans	X = CN Cis	X = CN Trans
1,3-Butadiene						
1-X	−250.475 33	−250.478 32	−607.018 81	−607.021 86	−243.571 98	−243.574 95
2-X	−250.476 56	−250.478 91	−607.017 56	−607.019 68	−243.568 41	−243.570 84
2,3-X_2	−347.931 51	−347.935 13				
Glyoxal						
2-X	−321.053 34	−321.054 38	−677.589 36	−677.590 96	−314.123 75	−314.125 69
2,3-X_2	−418.524 87	−418.525 20				
Acrolein						
2-X	−285.778 92	−285.778 90	−642.314 13	−642.313 03	−278.848 60	−278.848 29
3-X	−285.759 49	−285.758 32	−642.301 62	−642.300 92	−278.852 37	−278.851 76
4-X	−285.761 05	−285.761 00	−642.302 40	−642.302 40	−278.853 85	−278.854 05
2,3-X_2	−383.232 76	−383.232 32				

stable? How does the cis–trans energy difference change in the sequence butadiene, acrolein, and glyoxal, or when one of these three basic dienes is substituted? Finally what mode of stabilization is responsible for the distortion of the s-cis conformer away from planarity? This paper is an attempt to answer these questions. Let us point out immediately that arguments involving possible steric hindrance of hydrogen atoms (as in s-cis butadiene) or relating to in-plane lone-pair repulsions (as in s-cis glyoxal) will not be invoked here. The later, in particular, undoubtedly should,[9] but we decided instead to limit our discussion to the π manifold of orbitals. A clear understanding of the role played by the π system in dictating conformational preferences in dienes will facilitate the development of a more refined model including in-plane interactions.

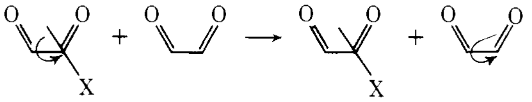
The π molecular orbitals of dienes and substituted dienes will be built up from those of simpler subsystems (double bonds and their substituted analogues) using the simple and natural Rayleigh–Schrödinger perturbation procedure.[10] This particular brand of perturbation theory (including overlap) has been developed by several authors.[11] Two types of MO interactions arise when both subsystems are in their closed-shell ground state. First a 4-electron interaction between doubly occupied MO's of each unit, which is net destabilizing, similar to that experienced between two approaching helium atoms. The destabilization energy is proportional to the square of the overlap, but independent of the energy gap, between the two interacting MO's. The second is a net stabilizing 2-electron interaction involving a doubly occupied MO on one subsystem and an empty one on the other. The stabilization energy is here again proportional to the square of the overlap of the combining MO's but, unlike the 4-electron term, is inversely so to their energy separation.

This qualitative orbital model will be documented quantitatively with theoretical ab initio molecular orbital calculations carried out using the GAUSSIAN 70 series of computer programs.[12] The geometries of the three basic skeletons we shall deal with (butadiene, acrolein, and glyoxal) have been fully optimized at the minimal STO-3G basis set level,[13] not only in their cis and trans conformations but also in various "gauche" geometries away from the planar cis form. These unsubstituted dienes are small enough to permit their energies to be obtained using the split-valance-shell 4-31G basis set,[14] the ability of which to accurately describe rotational potentials has been adequately documented in earlier publications.[15] Theoretical (STO-3G and 4-31G) energies for the three molecules in both cis and trans conformations are presented in Table I.

Structures for the fluoro, chloro, and cyano derivatives of 1,3-butadiene, acrolein, and glyoxal have been constructed by attaching the substituents to the optimized geometries of the parent molecules using "standard-model" bond lengths[16] (C–F = 1.33 Å; C–Cl = 1.71 Å; C–CN = 1.45 Å; C≡N = 1.16 Å). Although energy calculations at the minimal basis STO-3G level are quite feasible on these systems (and are given in Table II), because of the size of the molecules involved a complete study using the extended 4-31G basis set has not been possible. It is possible, however, to accurately simulate the results of the 4-31G calculations on the conformational preferences of the various substituted 1,3-dienes by combining the STO-3G energies of the *isodesmic*[17] reaction processes 1–3 with the



(1)



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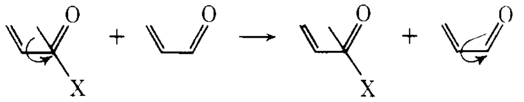


(3)

theoretical 4-31G potentials for rotation in the parent dienes. Basically, what we are asking here is that the STO-3G minimal basis set be capable of describing the subtle changes in conformational energies (relative to a cis structure) in going from parent to substituted molecules. Previous experience has indicated that such a demand is reasonable.[17]

I. Butadiene, Glyoxal, Acrolein

Let us first consider the interaction between the π systems of two isolated double bonds. For simplicity these two double bonds are composed of identical atoms (C═C double bonds), unsubstituted, and in their (π^2) closed shell ground states (Figure 1). We need only consider the 4-electron interaction 1 and the pair of 2-electron terms (interactions 2 and 3). We shall first demonstrate that all three effects favor a trans over

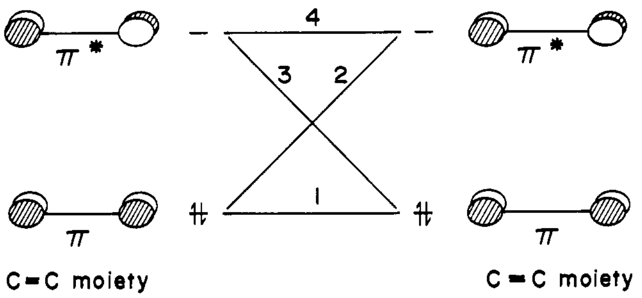
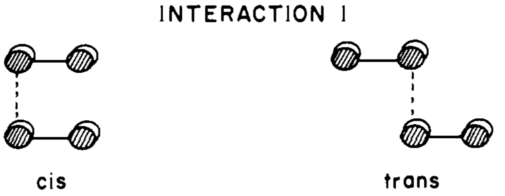


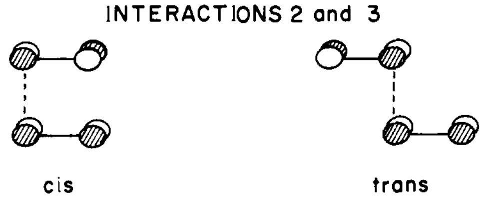
Figure 1. Interaction of the valence molecular orbitals of two carbon–carbon double bonds.



a cis skeletal arrangement of the two double bonds.[18]

Interaction 1 is 4-electron and net destabilizing. The cis conformer in which the positive overlap is greater than in the trans (that is, the overlap between the π lobes on the nonbonded terminal carbon atoms goes from a positive value in the cis conformer, to become vanishingly small in the trans arrangement) suffers the more in energy.

The single node introduced into the MO's which participate in the pair of stabilizing 2-electron interactions 2 and 3 is the cause behind their also favoring a trans orientation. In the cis arrangement a significant and negative secondary overlap of the orbitals on the terminal nonbonded atoms subtracts from the primary and positive overlap between the central pair of bonded atoms. Such an effect is largely absent in the trans form.



As shown in Table III ab initio calculations at the 4-31G split-valence-shell basis set level unambiguously confirm that the s-trans is the most stable conformer of 1,3-butadiene. The calculated cis–trans energy difference (3.40 kcal/mol) appears to be somewhat overestimated (by roughly 1 kcal/mol). The numerous other theoretical evaluations of this energy difference which have been carried out all fall in the range of 2–5 kcal/mol.[19]

Let us now consider how the π MO's of glyoxal are constructed from those of two identical C=O bonds. In this instance we have to contend with changes in the basic structure of the double bond orbitals resulting from the polar nature of the C=O linkage. Oxygen is more electronegative than carbon; therefore the π orbital will be heavily localized on the oxygen atom and π* on the carbon atom.

The energy difference between the two extreme cis and trans conformations is again determined by the secondary π overlaps between the terminal nonbonded (oxygen) atoms. Interaction 1 involves the larger lobes on the oxygen atom in π_{CO} and clearly results in a larger cis–trans separation in glyoxal as compared with butadiene. In the butadiene case interactions 2 and 3 were characterized by the overlap of two similar lobes on the terminal carbon atoms in π_{CC} and π_{CC}^*, respectively. These medium-sized lobes are now replaced by larger (on the oxygen end of the π_{CO} component) and smaller lobes (π_{CO}^* component).

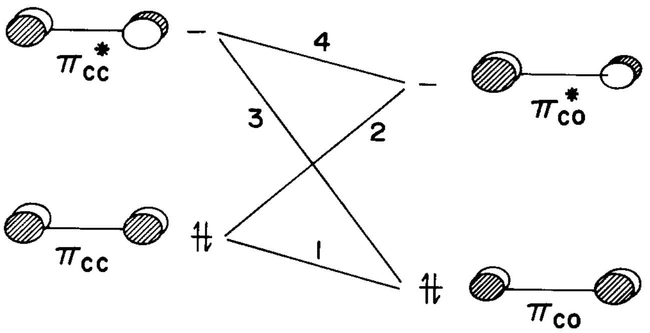


Figure 2. Interaction of the valence molecular orbitals of a carbon–carbon double bond with those of a carbonyl linkage.

Table III. E(cis) – E(trans) for 1,3-Butadiene, Glyoxal, and Acrolein (kcal/mol)

Molecule	Theoretical (4-31G)[a]	Exptl		
Butadiene	3.40	>2[2f]	2.3[2a]	1.7 ± 0.5[2e]
Glyoxal	5.40	3.2[4]		
Acrolein	0.80	2[3c]	2.09[3a]	

[a] Calculated from data given in Table I.

Thus, a clear-cut conclusion cannot be reached in the comparison of the cis–trans energy difference resulting from the pair of 2-electron terms in butadiene and glyoxal. It can only be said that they are probably similar. As a consequence the cis–trans energy separation in glyoxal should be greater than in butadiene the change being dictated by the increase of the cis secondary overlap in interaction 1. As is apparent in Table III both experimental and 4-31G ab initio evaluations confirm this prediction. (Other ab initio SCF calculations have found this energy gap to be 2.99[20] and 6.4 kcal/mol,[21] respectively).

Finally, let us examine the interaction of C=C and C=O double bonds (to form acrolein), Figure 2, as compared with, say, two ethylenes. Because oxygen is more electronegative than carbon, both the π_{CO} and π_{CO}^* MO's will be at lower energy than their π_{CC} and π_{CC}^* counterparts. For the same reason the π_{CO} orbital will reside primarily on oxygen while the π_{CO}^* function will be concentrated on carbon. Although interaction 1, which is independent of the energy difference between π_{CC} and π_{CO}, is slightly greater than it was for the case of two carbon–carbon double bonds (due to a localization of the π_{CO} orbital on the oxygen), the overiding factors, as far as any conformational preference goes, are the changes which occur in the 2-electron terms 2 and 3. Because the energy gap between π_{CC} and π_{CO}^* is now significantly smaller than that involving the complementary pair of orbitals, it is interaction 2 which takes the dominant role. Here, however, the antibonding π_{CO}^* orbital is localized mainly on carbon, reducing the importance of the secondary interaction between the diene termini. Thus, we would expect less of a preference for a trans ground state conformation here than we would in, say, 1,3-butadiene. The calculated cis–trans energy differences in acrolein (0.80 kcal/mol in the present work, 1,4 kcal/mol[22]) confirm our expectation.

We shall now proceed to investigate the consequences of distorting the diene skeleton away from a cis planar geometry.

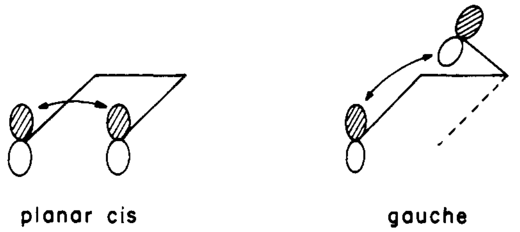
Table IV. Energies (4-31G Level) of Gauche Conformers of Butadiene, Glyoxal, and Acrolein Relative to Cis Forms (kcal/mol)[a]

	θ			
Molecule	0	15	30	60
Butadiene	0	−0.11	−0.44	0.49
Glyoxal	0	0.06	0.65	2.22
Acrolein	0	0.34	1.50	5.15

[a] θ is the angle of twist away from a cis planar form.

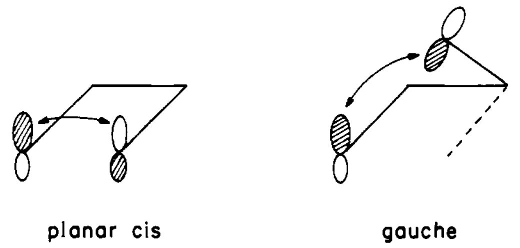
Of most significance will be a weakening of the (primary) π overlap between the directly σ bonded central pair of atoms. Although such a distortion is beneficial in reducing the magnitude of the 4-electron destabilizing term, the stabilizing character of the pair of 2-electron components 2 and 3 also decreases. On the other hand the (secondary) π components, those attributable to overlap between the diene termini and significant only in cisoid conformations, of all three interactions 1, 2, and 3 benefit from distortion away from planarity. Thus, the in-phase overlap between the terminal components of the two subsystem π orbitals is diminished by the twisting motion, thus reducing the overall destabilizing effect of interaction 1.

INTERACTION 1



At the same time, the corresponding out-of-phase overlap between the terminal components of the π and π^* orbitals in either of the equivalent 2-electron terms is increased, thus enhancing the net stabilization resulting from interactions 2 and 3.

INTERACTIONS 2 and 3



While it is apparent that the distortion of the diene to a gauche skeleton unquestionably diminishes the magnitude of the 4-electron destabilizing interaction 1 it should be noted that the primary (σ bonded) and secondary (terminal) components of the pair of 2-electron interactions 2 and 3 counteract one another.

Table IV suggests the possible existence of a second, gauche rotamer of butadiene whose energy is roughly 3 kcal/mol higher and 0.5 kcal/mol lower than those of the s-trans and s-cis rotamers, respectively. Although this secondary minimum has yet to be detected experimentally other calculations have already pointed out its possibility.[19a,d,23] However, no such gauche rotamer appears in either glyoxal or acrolein potential energy curves. To interpret these apparently conflicting behaviors two questions should be answered: how facile is the rotation around the central carbon–carbon bond in the three dienes, and what would each of them eventually gain as a result of such a distortion? The "strength" of the central bond depends mainly on the 4-electron interaction 1. The larger the primary overlap between the π lobes on the carbon atoms to be σ linked the larger the net destabilization caused by 1 and the weaker the central bond. Due to the decreased localization of the π orbital on the carbon atom when the ethylenic group is replaced by a carbonyl group we would expect the rotation to become more and more difficult in the sequence butadiene (two medium sized overlapping lobes), acrolein (one medium sized lobe on the ethylenic moiety and a "small" one on the carbonyl moiety), and, finally, glyoxal (two "small" lobes). Now the secondary negative overlap (between the termini) in interactions 2 and 3 is partly responsible for the destabilization of the cis conformer. During the torsion this overlap changes its sign to become positive and stabilizing. Butadiene and glyoxal clearly benefit from the distortion but acrolein, in which only interaction 2 remains, does so half-heartedly. To conclude we can say that butadiene is likely to adopt a gauche form because the movement is relatively easy and the profit certain. Acrolein and glyoxal remain the villains of the piece either because the torsion is difficult (glyoxal) or because the gain which would result is feeble (acrolein).

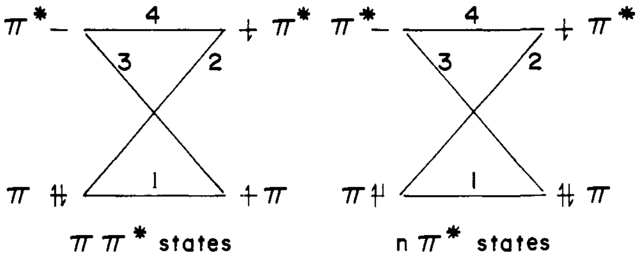
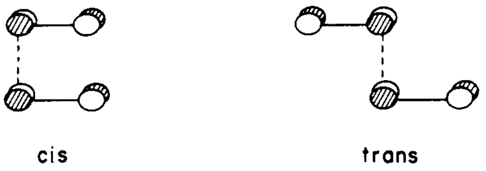


Figure 3. Interactions present in $\pi\pi^*$ and $n\pi^*$ states of 1,3 dienes.

To conclude this section we will now briefly consider the interesting problem of conformational preference in the $\pi\pi^*$ excited states of dienes. Here again the π MO's of two double bonds (subsystems) are brought near one another and interact to produce the π manifold of the diene. However, their electronic populations change. One of the subsystems remains in its (π^2) ground state but its partner is in an excited ($\pi\pi^*$) configuration (Figure 3). Interactions 1 and 2 are now 3-electron interactions. These are known to be neither stabilizing nor destabilizing. When two orbitals interact their antibonding combination is more destabilized than the bonding one is stabilized. Here, however, two electrons populate the bonding wave function and only one the antibonding. The two effects practically cancel each other. That 3-electron interactions are probably of little energetic consequence is evidenced by the conformational behavior of free-radical systems. For example, whereas the lone pair of a heteroatom prefers to eclipse the vacant p orbital at a carbonium center to which it is attached, and to remain perpendicular to the doubly occupied lobe of a carbanion, it exhibits only slight conformational preference when attached to a radical site.[24] Interactions 3 and 4 are 1-electron stabilizing. The first still favors the trans skeleton though to a much lesser extent than previously since a unique electron now intervenes. Interaction 4, a zero-electron term

INTERACTION 4



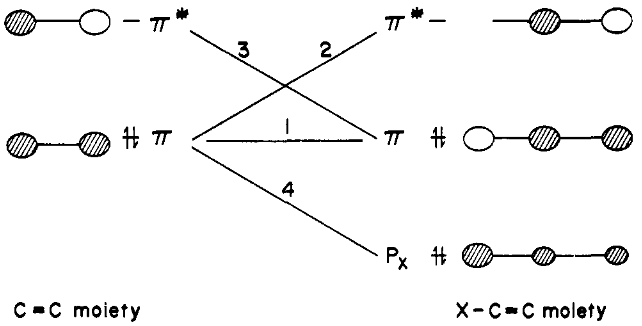


Figure 4. Interaction of the valence molecular orbitals of a carbon–carbon double bond with those on a substituted unsaturated carbon–carbon linkage.

Table V. E(trans) – E(cis) for the $\pi\pi^*$ Excited States of Butadiene, Glyoxal, and Acrolein (kcal/mol)

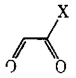
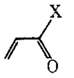
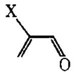
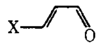
Molecule	Theoretical	Exptl
Butadiene		
$^1\pi\pi^*$	14.6[a]	
$^3\pi\pi^*$	2.07[a]	
Acrolein		
$^3n\pi^*$	2.4[b]	1.20[c]
$^1n\pi^*$	2.0[b]	1.50[c]
$^3\pi\pi^*$	2.2[b]	
Glyoxal		
$^1n\pi^*$	–2.25[3]	0.96[d]
$^1\pi\pi^*$	5.9[e]	

[a] R. Buenker and J. L. Whitten, *J. Chem. Phys.*, 49, 5381 (1968). [b] Reference 22. [c] E. J. Bair, W. Goetz, and D. A. Ramsay, *Can. J. Phys.*, 49, 2710 (1971). [d] Reference 4. [e] C. F. Dykstra and H. F. Schaefer III, *J. Am. Chem. Soc.*, **98**, 401 (1976).

in the case of ground state dienes, now becomes the decisive factor. Indeed it involves the strong combination of π^* components of equal (butadiene and glyoxal) or comparable (acrolein) energies. Two nodes have been introduced into the molecular orbitals derived from the interacting π bonding orbitals of the two subsystems and, consequently, the wave functions on the terminal atoms in the cis orientation overlap positively. This leads to a strong preference for cis over the trans forms. We would therefore expect the $\pi\pi^*$ excited states of dienes to adopt an s-cis conformation. Ab initio SCF–CI computations do agree with this statement (Table V). The 1-electron term 4 even remains dominant in the case of $n\pi^*$ excited states where the 4-electron term 1 and 2-electron term 3 favor, in a situation reminiscent of that encountered for the ground state, the trans conformer. Indeed the $n\pi^*$ states of acrolein and glyoxal have been experimentally (and, for acrolein, theoretically) observed to adopt a s-cis geometry opposite to the trans skeleton of their ground states.

II. Monosubstituted Dienes

Table VI. E(cis) – E(trans) for Monosubstituted Dienes (kcal/mol)[a]

	X			
Molecule	H	F	Cl	CN
	3.41	3.48	3.52	3.47
	3.41	3.08	2.94	3.13
	5.41	4.60	4.96	5.17
	0.82	0.40	–0.23	0.22
	0.82	–0.32	–0.03	0.03
	0.82	0.38	0.41	0.54

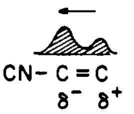
[a] Values are derived by correcting the 4-31G cis–trans energy differences of the parent molecules by the energies of the *isodesmic* processes 1–3 for the substituted butadienes, glyoxals, and acroleins, respectively.

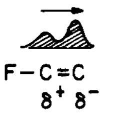
Table VII. Energies of Gauche Conformers of 1-Substituted Butadienes Relative to Cis (kcal/mol)[a]

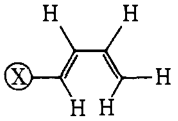
	θ		
X	0(cis)	15	30
H	0	–0.11	–0.44
F	0	–0.08	–0.41
Cl	0	–0.15	–0.53
CN	0	–0.09	–0.37

[a] Values are derived by correcting the 4-31G energy differences in parent 1,3-butadiene by the energy of the isodesmic process 1. θ is the angle of twist away from a cis planar arrangement.

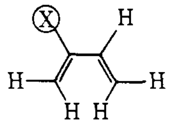
The substitution of one of the two interacting C=C or C=O double bonds with fluorine and chlorine atoms or cyano groups may be thought of as giving rise to three effects. The first one is the polarization of the ethylene and carbonyl linkages. A π-acceptor substituent (such as a cyano group) polarizes the double bond so that electron density accumulates on the substituted carbon atom. A π donor (such as a fluorine or a chlorine atom) produces the opposite polarization.[11d,16,25] The second effect results from the participation of the π lobes of the substituent (X) in interactions 1, 2, and 3. Finally these substituents are responsible for new interactions which were absent in the unsubstituted molecules. Let us examine successively these three factors. The importance of the polarization effect may be evaluated in the case of a 1-substituted butadiene. Here the X atom on the first subunit is far away from the unsubstituted partner and does not participate in interactions 1, 2, or 3. In addition the only novel interaction (4, see Figure 4 for its definition), which is due to an increase in the number of π MO's because of substitution, is extremely weak (this results from the very small contribution of both carbon atoms π orbitals to the lowest occupied MO p_x of the X—C=C unit). Any eventual change will therefore only result from polarization effects. The cis–trans energy differences (Table VI) as well as the energy changes upon rotation around the central bond away from the planar cis geometry (Table VII) are nearly the same in both unsubstituted and 1-monosubstituted butadienes. The polarization factor appears then to have only a slight effect on the conformation properties we are investigating here, and will be ignored henceforth. Let us now examine the 2-substituted butadienes (Figure 4). The participation of the π component on the X atom in the "old" interactions 1, 2, and 3 cannot be ignored any longer.







1-substituted butadiene



2-substituted butadiene

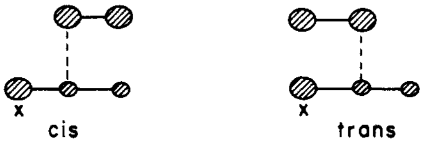
Interaction 1 again favors the trans conformer. However, the ensuing cis–trans energy gap is larger than in butadiene

INTERACTION 1

itself. In butadiene the positive secondary overlap (between the nonbonded terminal atoms) in the cis form vanishes upon rotation into a trans geometry. As the degree of energetic destabilization is proportional to the square of the net overlap, this term serves to disfavor the cis conformation. In the 2-substituted molecules, overlap between the termini goes from being positive in the cis geometry to negative in the trans. Therefore, consideration of this interaction alone leads us to conclude that such a pattern of substitution enhances the molecule's preference for a trans conformation. Interaction 2 does not change significantly upon substitution, for the coefficient on the substituent in the π^* orbital of the X—C=C unit is very small. Finally the stabilizing 2-electron term 3 not only favors the trans conformation but also results in a larger cis–trans energy separation than in butadiene itself. The mechanism for this parallels that already detailed for interaction 1. Here the negative secondary overlap in the cis form becomes positive in the trans. Not only is the cis form disfavored by a smaller net overlap (as in butadiene) but the trans conformation is more stabilized than in butadiene. The participation of the π component of X in both interactions 1 and 3 therefore results in a widening of the cis–trans energy gap in 2-substituted butadienes. The third effect, mentioned at the beginning of this section, remains to be considered. There appears to be only one new interaction: the 4-electron repulsion (interaction 4). The small secondary overlap in the cis form is replaced, upon rotation into a trans conformation, by a large overlap due to the quasi-complete localization of the lowest occupied MO of the X—C=C subunit (p_x) on the X atom. This new interaction strongly favors the cis geometry.

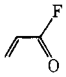
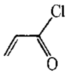
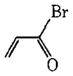
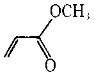
INTERACTION 3

INTERACTION 4



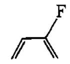
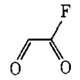
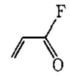
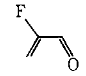
To conclude this study of 2-X-butadienes we may state that: (1) the polarization of the double bond has a negligible influence; (2) the X contribution to the "old" interactions 1, 2, and 3 increases, whereas (3) the "new" interaction 4 strongly decreases the cis–trans energy difference. Even though our qualitative arguments do not permit an unambiguous evaluation of the relative importance of these two counteracting tendencies it is not surprising, in view of the very large overlap which is responsible in interaction 4 for the destabilization of the trans form, that the overall result is a decrease of the cis–trans energy difference. This decrease, which is of the order of 0.5 kcal/mol, is clearly apparent for all the 2-substituted molecules listed in Table VI. Experimental results which could be used to calibrate our theoretical values are scarce. The cis–trans energy gap in 2-fluorobutadiene[6a,b] (and also in 2-methylbutadiene[6b]) is found (microwave studies) to be greater than 1 kcal/mol (vs. 3.08 kcal/mol in our calculations). As shown in Table VIII our theoretical results on acrolein derivatives compare particularly well with the reported experimental values when X = F. When X = Cl the difference is of the order of 0.8 kcal/mol. Table VI further shows that the calculated cis–trans energy difference narrows when the carbonyl group is substituted but decreases to an even larger extent when the ethylene unit is substituted. This is easily understood when we compare interaction 4 in both cases. Due to the localization of the π_{CO} orbital on the oxygen atom, the overlap which is responsible for the destabilization of the trans form is greater when we substitute the ethylenic moiety (X···O overlap, right-hand side) instead of the carbonyl partner (X···C overlap, left-hand side).

Table VIII. *E*(cis) – *E*(trans) for 2-Substituted Acrolein Derivatives (kcal/mol)[a]

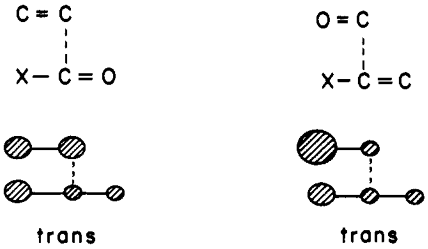
Molecule	Theoretical	Exptl		
	0.40	0.09[7d]	0.15[7e]	0.8[7f]
	−0.28	0.6[7g]		
		0.6[7g]		
		0.3[7h]		

[a] Theoretical values are derived by correcting the 4-31G cis–trans energy difference in parent acrolein by the energy of the *isodesmic* process 3.

Table IX. Energies of Gauche Conformers of Fluoro-Substituted Species Relative to Cis (kcal/mol)[a]

	θ		
Molecule	0°(cis)	15°	30°
	0	−0.15	−0.34
	0	−0.07	0.54
	0	0.37	1.53
	0	0.20	1.43

[a] Values are derived by correcting the 4-31G energy differences for parent molecules by the energies of the *isodesmic* processes 1–3 for the substituted butadienes, glyoxals, and acroleins, respectively. θ is the angle of twist away from a cis planar arrangement.



The tendency of cis dienes to distort away from planarity changes only marginally upon substitution. Table IX shows, for example, the energy changes during the first stages of

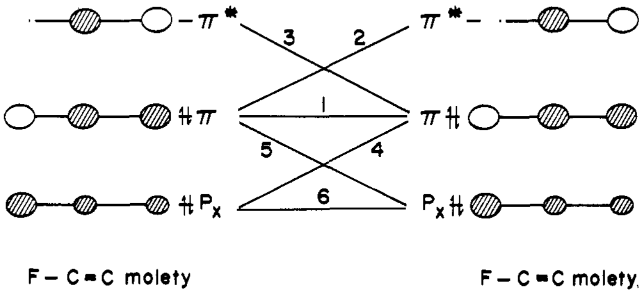


Figure 5. Interaction of the valence molecular orbitals on two fluorine-substituted carbon-carbon double bonds.

rotation around the central carbon-carbon bond for various fluoro dienes centrally substituted. Substitution of butadiene or of the carbonyl double bond of acrolein does not bring about any significant changes in the rotational potentials. Substitution of glyoxal or of the ethylenic unit of acrolein results in a meager additional stabilization of 0.2 kcal/mol. Still this effect is sufficient to induce a small distortion of the 2-fluoroglyoxal skeleton away from planarity. More generally 2-monosubstituted butadienes, like the parent molecule, appear to prefer gauche conformations ($\theta \simeq 30°$). 2-Monosubstituted glyoxals, unlike the s-cis parent, might also slightly distort ($\theta \sim 15°$). Although their potential energy surfaces do become flatter, 2-substituted acrolein derivatives prefer to maintain a planar s-cis geometry ($\theta = 0°$).

III. Disubstituted Dienes

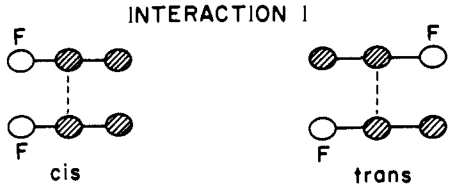
In this section we will mainly deal with 2,3-difluoro-substituted dienes. Rotational potentials for the analogous dicyano- and dichloro-substituted dienes have also been investigated using the quantitative molecular orbital procedures, although here conformations seem to be poorly described leading to cis-trans energy differences which are apparently much too large. Consider for example the cis conformation of 2,3-dichloroglyoxal. The geometrical structure used for the ab initio calculations here was, recall, based on that optimized for the unsubstituted system. Thus, the heavy-atom skeleton of the parent which was adjusted in order to minimize such factors as the repulsion between the oxygen lone pairs is no longer entirely appropriate for the chlorine-substituted molecule. In particular the lone pairs on the halogens probably repel each other to a greater extent than they would if complete geometrical optimization had been carried out on the substituted molecule. The dicyano-substituted system also suffers similarly from a lack of structural optimization. It is only the fluorine-substituted systems which come out unscathed, presumably due to the tight nature of the lone pairs here.

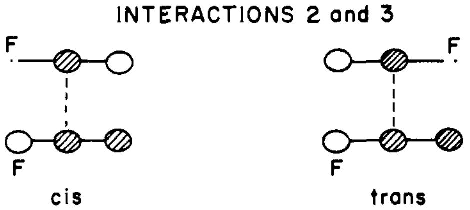
The π MO's of fluoroethylene result from the interaction of the π and π^* molecular orbitals of ethylene and the π lone pair of an isolated fluorine atom. This lone pair, however, does not appreciably mix with π_{CC}^* (their energy separation is too large) but does strongly so with the bonding π_{CC} counterpart. Usually the fluorine lone pair lies below π_{CC} and, as a result, their bonding combination is mainly located on the halogen atom (p_x) whereas the antibonding wave function is still largely concentrated on the double-bond moiety (hence its name, π). These three π molecular orbitals of the F—C=C fragment serve to perturbationally build up those of 2,3-difluorobutadiene as depicted in Figure 5.

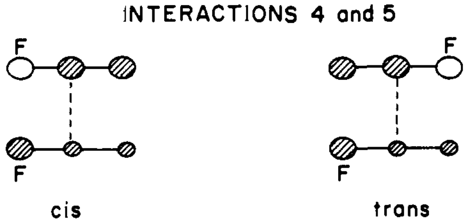
Let us examine the various interactions. The destabilizing 4-electron interaction 1 favors the trans rotamer, and results in a larger cis-trans energy difference than in either butadiene itself or 2-fluorobutadiene. Indeed two positive (and therefore strongly destabilizing) overlaps in the cis form (the usual secondary overlap between the terminal carbon atoms and the new F···F overlap) become negative in the trans form where they serve to diminish the overall destabilization. The stabilizing 2-electron interactions 2 and 3 also favor the trans form, and result in a cis-trans gap larger than in butadiene, since the secondary negative overlap in the cis form changes to positive in the trans form (recall that only interaction 3 was present in the 2-fluorobutadiene case). The "old" interactions therefore still stabilize the trans form and are responsible for a larger cis-trans gap than in either butadiene or its 2-fluoro analogue. Let us now consider the new interactions 4, 5, and 6. The pair of identical 4-electron terms 4 and 5 strongly favors the cis conformer. This is because the large F···F overlap is negative in the cis form and its F···C counterpart positive in the trans form. In the first case, this overlap diminishes the destabilization; in the second it reinforces it. (In the mono-substituted species, 5 was absent; 4 was present but "weaker".) Finally, interaction 6 (absent in all aforementioned cases) clearly favors the trans conformer. Note that 6 is the π analogue of the in-plane lone-pair repulsion. The effects of all these interactions on the cis-trans energy gap are collected in Table X. Recall that, in the 2-monosubstituted dienes, interaction 4 successfully counteracted interactions 1 and 3. As a result the cis-trans

Table X. Effect of the Various Interactions on the Cis-Trans Energy Gap in 2-Fluorobutadiene (as Compared with Butadiene) and in 2,3-Difluorobutadiene (as Compared with 2-Fluorobutadiene)

Interaction	2-Fluorobutadiene/ butadiene	2,3-Difluorobutadiene/ 2-fluorobutadiene
1	Larger	Larger
2	Similar	Larger
3	Larger	Similar
4	Smaller	Smaller
5		Smaller
6		Larger







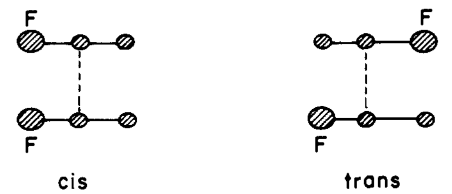
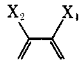
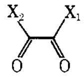
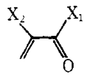
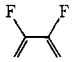
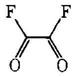
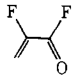


Table **XI.** E(cis) − E(trans) for 2,3-Disubstituted Dienes (kcal/mol)[a]

Molecule	$X_1 = X_2 = H$	$X_1 = F, X_2 = H$	$X_1 = X_2 = F$
	3.41	3.08	2.88
	5.41	4.60	4.17
	0.82	0.40	0.14

[a] Values are derived by correcting the 4-31G cis–trans energy differences of the parent molecules by the energies of the *isodesmic* processes 1–3 for the substituted butadienes, glyoxals, and acroleins, respectively.

Table **XII.** Energies of Gauche Conformers of 2,3-Difluoro-Substituted 1,3-Butadiene, Glyoxal, and Acrolein Relative to Cis Forms (kcal/mol)[a]

	θ			
Molecule	0	15	30	60
	0	−0.28	−0.56	−0.18
	0	−0.24	0.32	1.59
	0	0.25	1.48	4.96

[a] Values are derived by correcting the 4-31G energy differences for the parent molecules by the energies of the *isodesmic* processes 1–3 for the substituted butadienes, glyoxals, and acroleins, respectively. θ is the angle of twist away from a cis planar form.

energy difference in these species was smaller than that in the unsubstituted parents. In a similar fashion, interactions 4 and 5 in the 2,3-difluorosubstituted dienes seem to completely erase interactions 1 and 2 (and 6), and to further decrease the cis–trans energy gap. The regular decrease of this gap upon successive fluorine substitution of the central bond is clearly evidenced in Table XI for all three series of dienes. Comparison of these trends with experimental results is not possible at the present time. Still indirect checks are available and will be discussed at the end of this paragraph.

The tendency for the s-cis conformer to distort away from planarity increases slightly upon substitution in the butadiene and glyoxal derivatives, not significantly in the acrolein analogues. Though small (0.2 kcal/mol), the stabilization thus received might be sufficient for oxalyl fluoride to adopt a gauche geometry. Oxalyl chloride[8a] and bromide[8b] have indeed been found to exhibit stable gauche rotamers (of course the trans rotamer is still the most stable conformer). In both cases the angle of torsion, as determined experimentally, is 63°. The calculated values for oxalyl fluoride and chloride are approximately 15 (see Table XII) and 50°, respectively. Moreover these experimental results might allow us to check our calculations. The experimental cis–trans energy difference in glyoxal itself is 3.2 kcal/mol.[4] The gauche-trans separations are 1.38 kcal/mol and 0.6 kcal/mol in glyoxal chloride[8a,26] and bromide,[8b] respectively. We might, therefore, reasonably expect the gauche-trans gap in fluoride to be of the order of 2.2 kcal/mol. Now the (4-31G) calculated difference for glyoxal itself is clearly 2.2 kcal/mol too large (5.4 kcal/mol vs. 3.2 kcal/mol experimentally[4]). This correction should hold for glyoxal fluoride and would bring the theoretical gauche-trans separation from 4 kcal/mol down to 1.8 kcal/mol, a result clearly in the range of the experimental evaluation.

Conclusion

We have investigated the conformational properties of conjugated dienes using single determinant ab initio molecular orbital theory. Our results are generally in good agreement with the available experimental values, qualitatively as well as numerically. The following points are especially worthy of note: In all cases the planar s-trans form was found to be the most stable conformer (this fact is also well established experimentally). As far as the second stable isomer is concerned two possibilities appear. This conformer may retain a planar s-cis geometry (acrolein and its various derivatives or glyoxal itself) or distort away from planarity. (This is the case for substituted glyoxals or butadiene and its derivatives.) Gauche butadiene has yet to be detected experimentally but oxalyl chloride and bromide are known to exhibit a second gauche rotamer. The calculated cis–trans (or, eventually, gauche-trans) energy differences agree well with reported experimental values (monosubstituted acrolein) or fall within 1 or 2 kcal/mol of them (glyoxal and butadiene). These energy separations increase from acrolein (0.8 kcal/mol) to butadiene (3.4 kcal/mol) and glyoxal (5.4 kcal/mol) and decrease regularly upon successive substitutions of the central carbon–carbon bond. Our use of the results of perturbation theory to rationalize these effects suggests the following remarks: Although we have ignored the (in-plane) lone-pair repulsions and purposely based our arguments only on the π manifold of molecular orbitals, the various effects detected in the case of the unsubstituted dienes (whether in their ground state or in a $\pi\pi^*$ excited state) and, to a lesser extent, of the monosubstituted parents are successfully explained. This is mainly because the number of interactions to be considered is small (three or four). On the other hand, this number increases to six in the disubstituted species, making conclusions rather difficult. (Indeed we had to use the calculated energy differences to decide which interaction(s) were the decisive ones!) This study clearly delineates a frontier beyond which perturbation molecular orbital theory as applied to conformational analysis becomes ambiguous. Problems involving a small number of atoms (from 2 to 5) interactions (3 or 4) are usually elegantly solved. Should, however, the number of interacting centers be stretched beyond that limit (6 in our difluoro dienes), and therefore the number of conflicting influences, then it is our opinion that clear-cut decisions regarding conformations cannot usually be extracted from the simple perturbation molecular orbital model.

References and Notes

(1) (a) University of Paris; (b) the Laboratoire de Chimie Organique Theorique is associated with the CNRS (ERA 549); (c) Concordia University; (d) University of California, Alfred F. Sloan Fellow 1974–1976.

(2) (a) J. G. Aston, G. J. Ssasz, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946); (b) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958); (c) M. Batuev, A. Onishchenko, A. Matveeva, and N. I. Azonova, *Dokl. Chem.* (*Engl. Transl.*), 543 (1960); (d) D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 163 (1962); (e) E. B. Reznikova, V. I. Tulin, and W. M. Tatevskii, *Opt. Spektrosk.*, **13**, 200 (1969); (f) S. Novick, J. M. Lehn, and W. Klemperer, *J. Am. Chem. Soc.*, **95**, 8189 (1973).

(3) (a) M. S. DeGroot and J. Lamb, *Proc. R. Soc. London, Ser. A*, **242**, 36 (1957); (b) E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, **45**, 104 (1966); (c) A. C. P. Alves, J. Christoffersen, and J. M. Hollas, *Mol. Phys.*, **20**, 625 (1971).

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Nucleophilic Additions to Phosphine Oxides. A Model Study of Anionic Trigonal Bipyramidal Intermediates

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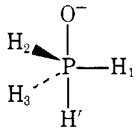
Abstract: $POH_3 + H^-$ has been used as a model to ascertain whether the phosphoryl oxygen will be more stable axial or equatorial compared with the alkyl groups in anionic trigonal bipyramidal transition states or intermediates formed via nucleophilic additions to phosphine oxides. Ab initio electronic structure calculations were carried out for a variety of geometries and we find that the trigonal bipyramid with the phosphoryl oxygen *equatorial* is more stable. This conclusion is in disagreement with the previously suggested order of preference for an axial site in a trigonal bipyramid, $OR(H) > O^- > CH_3$. We also find that the transition states or intermediates will be distorted trigonal bipyramids. The principal origin of equatorial preference derives from a symmetry controlled charge delocalization in the antibonding π orbitals. The π-donor repulsion effect and phosphorus d-orbital participation also favor an equatorial site, but they are of lesser importance.

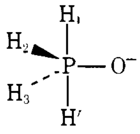
I. Introduction

Nucleophilic additions to phosphorus-oxygen bonds are an important aspect of organic chemistry and biochemistry. Most nucleophilic additions to tetrahedral phosphorus compounds are believed to proceed via a trigonal bipyramidal (TBP) transition state or intermediate.[1] The most stable pseudorotamer of the TBP anions formed in the alkaline exchange or racemization reactions of phosphine oxides ($POR_1R_2R_3$) has remained unresolved and a principal purpose of this paper is to answer this question.

The preference rules which have been proposed for deciding the placement of ligands in a TBP are: (1) the entering nucleophile and the most electronegative ligand should occupy the axial positions;[1-6] (2) π donors prefer to occupy equatorial sites.[7] Both a phosphoryl oxygen and an alkyl group are recognized as being very electropositive species and would thus tend to occupy an equatorial site.[1-6] However, in a TBP formed via nucleophilic addition to a phosphine oxide, either the phosphoryl oxygen or an alkyl group must occupy the second axial site. The order of preference for the axial sites in a TBP given by Richards and Wyckoff,[8] $OR(H) > O^- > CH_3$, suggests that the TBP with the incoming nucleophile and the O^- axial will be the more stable transition state or intermediate in these reactions. In contrast, the large negative charge on the phosphoryl oxygen makes it an efficient π donor which suggests that the more stable TBP will have the nucleophile and an alkyl group axial. In order to ascertain which of these trigonal bipyramids is more stable we have carried out ab initio electronic structure calculations for species I, symmetry C_{3v}, and II,



TBP I (C_{3v})



TBP II (C_{2v})

symmetry C_{2v}. Here the nucleophile is H′ and is constrained to occupy one of the axial sites. The relative stabilities of these