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Molecular Structure and Electronic Properties of $CF_3C{\equiv}SF_3$

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Abstract: The molecular structure and electronic properties of $CF_3C{\equiv}SF_3$ have been calculated by using a double-ζ basis set augmented by sets of polarization functions on both C and S. A short, polar C≡S bond (1.412 Å) and a linear C—C≡S geometry were found for the lowest energy structure. The bond length agrees with the experimental single-crystal structure, but the bond angle differs by 8.5°. A bent C_s structure with a C—C≡S bond angle of 171.6° was found to be only 210 cal/mol higher in energy, however. The vibrational frequencies and infrared intensities for $CF_3C{\equiv}SF_3$ also were calculated and a very low frequency of 77 cm^{-1} for the CCS bending vibration is predicted. A large amplitude of about 6° for the zero-point bending motion is indicated, and the excited $v = 1$ state for the CCS bend is calculated to be significantly populated at the temperature used for the crystal structure determination. Very small crystal-packing forces thus could easily account for the observed nonlinear C—C≡S geometry in the solid state. The $CF_3C{\equiv}SF_3$ molecule has a calculated ionization potential of 12.87 eV and a dipole moment of 1.21 D.

The molecule $CF_3C{\equiv}SF_3$ is unique because it is the first species with a C≡S triple bond. The molecule recently has been synthesized and structurally characterized by X-ray diffraction methods.[1] It reportedly has three novel structural features: a short C—C bond (r = 1.418 ± 0.021 Å), a short C≡S bond (r = 1.398 ± 0.015 Å), and a nonlinear CCS framework (θ(CCS) = 171.5 ± 6°) where the error limits are given as 3σ. A recent ab initio calculation[2] on $CF_3C{\equiv}SF_3$ predicted short C—C and C≡S bonds in reasonable agreement with experiment but indicated that the CCS framework should be linear. Thus, it is unclear whether the slightly nonlinear CCS experimental geometry represents the true molecular structure or results from solid-state effects.

We have been interested in studying the structure and properties of a wide variety of fluorocarbons using the techniques of molecular orbital theory.[3] For diverse fluorocarbon structures, we have found that a double-ζ basis set augmented by d functions on carbon (DZ+D(C)) usually gives very accurate bond angles and bond lengths; all bond lengths are consistently shorter than experiment. This is typical of calculations at the SCF level with near Hartree–Fock basis sets.[4]

It is well-known that the neglect of polarization in double-ζ basis sets results in bond angles that are too large. For instance, the calculated bond angle in H_2O is too large by 8°,[5] and NH_3 is calculated to be planar.[6] Moreover, polarization functions on multiply bonded atoms are often crucial for accurate calculations of equilibrium geometries.

The 4-21G basis set previously used to calculate the geometry of $CF_3C{\equiv}SF_3$ included d functions on S but not on C. The predicted linear C—C≡S geometry therefore might be in error because of a basis set deficiency. To examine this possibility, we have calculated the structure of $CF_3C{\equiv}SF_3$ by using a double-ζ basis set augmented by d functions on *both* C and S (DZ+D(C,S)). We also have calculated the vibrational frequencies and infrared intensities for this molecule.

Table I. Geometry Parameters for $CF_3C{\equiv}SF_3$[a]

SCF (C_s)[b]		SCF (C_{3v})[b]	SCF (C_{3v})	exptl[c]
parameter	this work	this work	ref 2	ref 1
r(C–S)	1.414	1.412	1.404	1.398 (15); 1.420
r(C–C)	1.473	1.469	1.435	1.418 (21); 1.439
r(S–F_3)	1.565	1.568	1.552	1.527 (33); 1.568
r(S–F_4)	1.569	1.568	1.552	1.550 (30); 1.568
r(S–F_4')	1.569	1.568	1.552	1.536 (9); 1.568
r(C–F_1)	1.322	1.323	1.360	1.304 (57); 1.360
r(C–F_2)	1.324	1.323	1.360	1.335 (54); 1.360
r(C–F_2')	1.324	1.323	1.360	1.332 (21); 1.360
θ(CCS)	171.6	180.0	179.9	171.5 (60)
θ(CSF_3)	122.6	123.6	123.3	119.7 (33)
θ(CSF_4)	124.2	123.6	123.3	124.9 (9)
θ(CSF_4')	124.2	123.6	123.3	124.6 (33)
θ(CCF_1)	112.2	111.4	111.9	108.8 (45)
θ(CCF_2)	111.1	111.4	111.9	111.8 (15)
θ(CCF_2')	111.1	111.4	111.9	115.6 (42)

[a] Bond distances in Å. Bond angles in degrees. [b] Total energy = −1069.727 270 au (C_s), −1069.727 610 au (C_{3v}). [c] First entry is the value calculated from atomic coordinates and isotropic thermal parameters. Error limit (3σ) in parentheses. Second entry is the value corrected for anisotropic thermal vibrations.

Calculations

The geometry of $CF_3C{\equiv}SF_3$ was determined with the program HONDO[7] on an IBM 3081 computer system. Gradient techniques[8] were used to obtain the optimum geometry. The calculations were done with a double-ζ basis set augmented with sets of d functions on C and S. The coefficients and exponents were taken from Dunning and Hay[9] (α_d(S) = 0.6); the basis set has the form (11s7p1d/9s5p1d/9s5p)/[6s4p1d/3s2p1d/3s2p] for the order S/C/F. Subsequent calculations on the vibrational frequencies were done analytically with the program GRADSCF[10] on a CRAY XMP/48 equipped with a solid-state disk (SSD). The vibrational frequencies and infrared intensities were both calculated analytically.[11] For these calculations, a basis set of the form (12s9p1d/9s5p1d/9s5p)/[6s4p1d/4s2p1d/4s2p] was used with coefficients and exponents for the double-ζ basis set for S from McLean and Chandler[12] and for C and F from Dunning.[13] The exponents for the d

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(1) Potter, B.; Seppelt, K.; Simon, A.; Peters, E. M.; Hettich, B. *J. Am. Chem. Soc.* **1985**, *107*, 980.

(2) Boggs, J. E. *Inorg. Chem.* **1984**, *23*, 3577.

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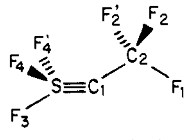
functions are those given above. There are 116 basis functions in this calculation.

Results and Discussion

Geometries. The geometry of $CF_3C{\equiv}SF_3$ was initially optimized in the solid-state conformation given below[14] beginning with a value for θ(CCS) of 171.5°. The structure was converged to a maximum variation of 0.0006 Å in any coordinate. This gave a value for θ(CCS) of 171.6°, and the remaining geometric parameters are given in Table I. The force field at this geometry (see below) did not give any imaginary frequencies for the CCS bend. These geometric parameters then were used to derive a C_{3v} structure with a linear C—C≡S moiety in the conformation given below. This structure was lower in energy by 0.09 kcal/mol. The



C_{3v} structure subsequently was optimized to ±0.0005 Å in any coordinate, and it proved to be 0.21 kcal/mol lower in energy than that the bent (C_s) structure. The optimum parameters for the C_{3v} structure are given in Table I.

Other than the value of θ(CCS), there are only small differences between the C_{3v} and C_s structures. The C≡S and C—C bonds are shorter by 0.004 and 0.002 Å, respectively, in the linear (C_{3v}) form. These differences are consistent with the change in hybridization of C_1. The values for r(S–F), r(C–F), θ(CSF), and θ(CCF) in the C_{3v} form correspond exactly to the average values of those parameters in the C_s form.

The calculated values for r(C–S) and r(S–F) in either the C_{3v} or C_s form are slightly longer than the average experimental values (uncorrected for anisotropic thermal vibrations). This is typical of SCF calculations of bond distances between first- and second-row atoms.[15] As expected from our previous studies[3] and the work of others,[16] the calculated C–F bond lengths are slightly shorter than the experimental values. The average of the experimental CCF bond angles is 112.1°, which is in excellent agreement with the theoretical value of 111.4° for the C_{3v} structure. The calculated value for $\theta(CCF_1)$, however, is 2.6° larger than the average experimental angle (108.8°) but is within the upper limit of experimental uncertainty (±4.5°) for this bond angle. Bending the CCS angle to 171.6° increases the calculated value for $\theta(CCF_1)$ to 112.2°. Since this level of theory ordinarily gives bond angles in excellent agreement with experiment, the actual value for $\theta(CCF_1)$ is likely to be much closer to 111° than to 108°. The two equivalent CCF bond angles (111.4°) agree well with the average experimental value for $\theta(CCF_2)$, 111.8°. The reported $CCF_{2'}$ angle (115.6°) is undoubtedly too large, and notably, the experimental uncertainty for this angle is ±4.2°.

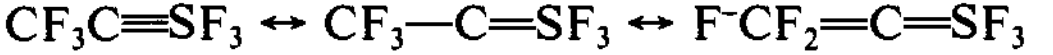
The average of the experimental values for θ(CSF), 123.1°, is in excellent agreement with the calculated value. Bending of the CCS angle is predicted to increase the two equivalent CSF bond angles and to decrease the unique CSF angle. The experimental values are larger than the changes predicted by theory. This is especially true for the unique CSF_3 bond angle, which is calculated to be 2.9° larger than the average experimental value but again is within the uncertainty limit (±3.3°). The FSF bond angles are calculated to be 92.4° for the C_{3v} structure ($\theta(F_3SF_{4,4'})$ = 92.3°, $\theta(F_4SF_{4'})$ = 92.2° for the C_s structure), which is consistent with the experimental values of 90.9–94.3°.[1]

There is reasonable agreement between the previous theoretical geometry[2] and our results for the above parameters. The bond angles differ by less than 1°. The C–F bond lengths determined with the 4-21G basis set are significantly longer than our values (and experiment), which is consistent with previous findings.[16] By contrast, the S–F bond lengths determined by Boggs[2] are slightly shorter than our calculated values. Most significantly, both Boggs' and our results predict a linear C—C≡S geometry in disagreement with the X-ray experimental results. The peculiar dynamic properties that account for this discrepancy are discussed in the following sections. In the remainder of this section, the theoretical and experimental results for the C—C bond length in $CF_3C{\equiv}SF_3$ are discussed.

The calculated value for r(C–C) is 0.051 Å longer (0.055 Å longer for the C_s structure) than the average experimental value. The magnitude of this difference is much larger than that usually found for single bonds between first-row atoms at this level of theory; furthermore, the error is in the wrong direction. To ascertain if this difference results from a failure of our basis set to adequately handle C—C≡ bonds, we calculated the structure of hexafluoro-2-butyne, $CF_3C{\equiv}CCF_3$. With our basis set (DZ+D(C)), the optimized value for r(C–C) is 1.483 Å, which compares to the experimental value of 1.472 (6) Å.[17] This demonstrates the quality of our basis set in treating this type of C–C σ bond. In fact, our calculated value for r(C—C) in $CF_3C{\equiv}SF_3$ is similar to that found in $CF_3C{\equiv}CCF_3$ and other C—C≡X derivatives.[18]

Careful consideration of the thermal motion of the atoms in the crystal and the precision of the structure determination provides some insight into the discrepancy between theory and experiment for r(C–C). Correcting the C–C distance for thermal effects[1] gives r(C–C) = 1.439 Å. When the usual uncertainty for crystal structure analyses (3σ) is included, an upper limit to r(C—C) becomes 1.460 Å. The calculated vs. experimental structure for hexafluoro-2-butyne shows that the calculation at the DZ+D(C) level overestimates the C–C bond length by 0.011 Å. If this difference is used as a correction factor for the C—C bond length in $CF_3{\equiv}SF_3$, a corrected calculated value of 1.458 Å is obtained. This agrees well with the upper range of experimental values, and we suggest that 1.460 Å is a more appropriate value for r(C–C). The C—C bond length in $CF_3C{\equiv}SF_3$ is not abnormal in comparison to other CF_3—C≡ bond lengths.[17-20]

The reportedly short C–C bond has been attributed to the presence of negative anionic fluorine hyperconjugation (resonance hybrid **1b**). Significant resonance of this type would lead to



$$CF_3C{\equiv}SF_3 \leftrightarrow \underset{\mathbf{1a}}{CF_3{-}\overset{-}{C}{=}\overset{+}{S}F_3} \leftrightarrow \underset{\mathbf{1b}}{F^-CF_2{=}C{=}\overset{+}{S}F_3}$$

abnormally long C–F bonds. The calculated and average experimental C–F bond lengths in $CF_3C{\equiv}SF_3$, however, do not differ significantly from those in $CF_3C{\equiv}CH$ (1.337 (1) Å), $CF_3C{\equiv}CCl$ (1.336 (6) Å), $CF_3C{\equiv}CCF_3$ (1.333 (3) Å), or other compounds containing the CF_3 group.[21] Furthermore, the calculated FCF bond angles (107.4°)[22] are comparable to those in $CF_3C{\equiv}CH$ (107.5 (10)°),[19] $CF_3C{\equiv}CCF_3$ (108.1 (3)°),[17] and other CF_3 derivatives.[21] If enough anionic hyperconjunction was present to actually shorten the C—C bond in $CF_3C{\equiv}SF_3$ by 0.051 Å from its nominal value in $CF_3C{\equiv}CCF_3$, not only should the C—F bonds lengthen significantly but also the FCF bond angles should contract noticeably. Consider, for example, the carbanions $CF_3CF_2^-$ and $CF_3CH_2^-$ in which anionic hyperconjunction plays a significant role.[3,23] At the DZ+D(C) level, which we have

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(14) The DZ+D(C,S) calculations find that the eclipsed conformation shown is more stable than the staggered conformation by 340 cal/mol. The previous ab initio calculations[2] found the staggered form to be more stable by 35 cal/mol.

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(18) For $CF_3C{\equiv}CH$, r(C—C) = 1.465 (2) Å;[19] for $CF_3C{\equiv}CCl$, r(C—C) = 1.453 (2) Å.[20]

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(22) The average values calculated from the experimental data in Tables III and IV in ref 1 are $\theta(F_2CF_{2'})$ = 108.9°, $\theta(F_1CF_{2'})$ = 108.2°, and $\theta(F_1CF_2)$ = 102.7°. The last value obviously is not correct.

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Table II. Calculated Harmonic Vibrational Frequencies and Infrared Intensities for $CF_3C\equiv SF_3$

C_{3v} ω, cm^{-1}	C_{3v} I, km/mol	C_s ω, cm^{-1}	C_s I, km/mol
77 (e)	0.2	82	0.3
		85	0.3
303 (e)	3.5	301	3.0
		304	3.9
351	7.0	350	7.3
428 (e)	14.8	428	13.5
		431	15.8
503 (e)	8.1	502	8.4
		507	7.7
594	61.8	595	61.2
655 (e)	12.2	652	11.6
		657	12.7
796	190	796	188
852 (e)	235	846	241
		858	227
933	286	932	284
1353 (e)	443	1345	363
		1348	442
1354	315	1356	397
2051	639	2033	639

Table III. Electronic Properties of $CF_3C\equiv SF_3$ (C_{3v})

atom	atomic charges q, e	atom	atomic charges q, e
S	+1.38	$F_{1,2,2'}$	−0.18
C_1	−0.57	$F_{3,4,4'}$	−0.31
C_2	+0.68		

	HOMO charge distribution	
orbital	I.P., eV	charges, e
HOMO	12.87	C_1 (1.18); S (0.54)

shown adequately treats the geometical consequences of anionic hyperconjunction in perfluorinated carbanions[3] and alkoxides,[24] the C–C and C–F_β bonds in $CF_3CF_2^-$ are, respectively, 0.01 Å shorter and 0.03–0.04 Å longer than those in CF_3CF_3, and the $F_\beta CF_\beta$ angles are 4–5° smaller than that in CF_3CF_3. Similarly, the C–C and C–F bonds are 0.06 Å shorter and 0.03–0.08 Å longer, respectively, in $CF_3CH_2^-$ than those in CF_3CH_3, and the FCF angles contract 2–7°. Since the geometry of the CF_3 group in $CF_3C\equiv SF_3$ is normal, it is evident that anionic hyperconjunction in this molecule is negligible. This further supports our contention that the C–C bond should not be abnormally short and its actual length corresponds to the upper limit of the experimental values (1.460 Å).

Vibrational Frequencies. The vibrational frequencies and infrared intensities that were calculated for both the optimum C_{3v} and C_s structures are listed in Table II. We report 20 vibrational frequencies. The structure should have 21 vibrational modes. However, there is essentially a free rotation of the CF_3 group that is strongly coupled to the overall molecular rotations, giving 20 vibrational modes. This rotational frequency is imaginary with a value of 30 cm^{-1} and suggests that the optimum structure may be C_3 rather than C_{3v}. The other six modes corresponding to translation and rotation are at zero frequency. This is consistent with the spectral features of 2-butyne[25] and hexafluoro-2-butyne[26] which exhibit 23 vibrational modes instead of the expected 24. The eight highest frequency modes are quite intense and should be easily observable in the infrared. The calculated frequencies, however, are probably all about 10% too high because of the neglect of correlation corrections and anharmonic effects.

The highest mode at 2051 cm^{-1} is assigned to the C≡S stretch. We assign the next three modes (1354, 1353 (e) cm^{-1}) to C–F stretches. For comparison, the C—F stretches in $CF_3C\equiv CH$ are at 1254 and 1182 (e) cm^{-1}.[26] The next four modes comprise the S–F stretches and the C–C stretch. Clearly the degenerate modes at 852 cm^{-1} are S–F stretches, and the mode at 933 cm^{-1} is predominantly an S–F stretch. The experimental values for $N\equiv SF_3$[27] are 811 (e) and 775 cm^{-1} by comparison. The predicted value for the C–C stretch (796 cm^{-1}) is in line with the values found for $CF_3C\equiv CH$ (810 cm^{-1}),[26] $CF_3C\equiv CCl$ (937 cm^{-1}),[28] and $CF_3C\equiv CCF_3$ (771, 900 cm^{-1}).[26] The large intensities for these frequencies are consistent with the polar nature of the bonds. The degenerate lowest frequency modes at 77 cm^{-1} are assigned to the two CCS bonding vibrations. For comparison, the CCC bending modes appear at 171 (e) cm^{-1} in $CF_3C\equiv CH$ and at 186 (e_g), 75 (e_u) cm^{-1} in $CF_3C\equiv CCF_3$.[26]

Bending the CCS angle does break the degeneracies but does not significantly affect the frequencies (Table II). The largest change is found for the C≡S stretch, which decreases by 18 cm^{-1} on bending and is consistent with the slight increase in the C≡S bond length. Bending the CCS angle by 8.4° leads to an increase in the CCS bending frequencies of only 5 and 8 cm^{-1}. The potential energy surface for bending is very flat in this region, and the bending frequencies are not strongly dependent on the value of θ(CCS). The only intensities that change on bending are those for the C–F stretches. The intensity for the highest energy C–F stretch increases by ca. 25% and that for the lowest decreases by a comparable amount.

Linear vs. Bent C—C≡S Geometry. The calculated value for θ(CCS) is 8.5° larger than the value observed in the crystal, which has a large uncertainty of 6°. Our results clearly demonstrate that the bent structure is higher in energy than the C_{3v} form, albeit by only 210 cal/mol. To gain more information about the potential energy surface for θ(CCS) between 170° and 180°, the convergence criteria for the gradient were tightened up and the C_s structure was further optimized. The surface is very flat, and convergence thus is very slow. The calculations were discontinued at $\theta(CCS) = 173.5°$. This structure is 80 cal/mol lower in energy than that with $\theta = 171.6°$ and only 130 cal/mol above the most stable C_{3v} structure ($\theta = 180°$).

The low frequency for the CCS bend provides insight into the difference between the observed and calculated values for θ(CCS). The zero-point frequency for the CCS bending motion is approximated as one-half of the calculated bending frequency. The resultant value of 38.5 cm^{-1} (110 cal/mol) is not exact since the harmonic approximation evaluated at the optimum C_{3v} structure is used, but it should be a reasonable estimate. From the relative energy of the structure with $\theta(CCS) = 173.5°$ ($\Delta E = 130$ cal/mol), a large amplitude of 6° for zero-point motion is indicated. This corresponds precisely to the 3σ uncertainty in the experimental value for θ(CCS).

If the molecule is excited to the $v = 1$ state for the CCS bend (220 cal/mol), an even larger bending amplitude will be observed and the experimental single-crystal value for θ(CCS) clearly is within these limits. At room temperature ($kT = 600$ cal/mol), there is significant population of the $v = 1$ state for the CCS bend, and even at the −130 °C temperature used for the crystal structure measurements, the vibrational frequency for the CCS bend is still less than kT. These results indicate that there will be large amplitude motions in the CCS bend under conditions at which most experimental measurements are made. Moreover, very small crystal-packing forces could easily account for the 8° deviation of θ(CCS) from linearity in the solid state.[29]

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(29) It is possible that including electron correlation in the SCF calculations may result in a bent structure that is more stable than the C_{3v} form. To date, however, propadienone is the only reported case in which electron correlation is needed to correctly predict the symmetry of the equilibrium structure; see: Brown, R. D.; Champion, R.; Elmes, P. S.; Godfrey, P. D. *J. Am. Chem. Soc.* **1985**, *107*, 4109 and references cited therein. To properly demonstrate the effects of electron correlation in $CF_3C\equiv SF_3$, a CI-SD, MP4, or CASSCF calculation should be done. Considering the size of our basis set and the number of electron pairs in the molecule, any of these calculations is clearly beyond our present capabilities.

Electronic Properties. Various electronic properties of CF_3-$C\equiv SF_3$ are summarized in Table III. The molecule has a calculated ionization potential of 12.87 eV for a degenerate orbital. The degenerate HOMOs are composed of predominantly the π part of the $C\equiv S$ bond. The orbitals are strongly polarized toward carbon with 1.18 e on C and 0.55 e on S. The charge distributions are as expected. The fluorines are negatively charged, whereas the carbon in the CF_3 group and the sulfur are positively charged. The fluorines bonded to carbon have a significantly lower negative charge than those bonded to sulfur. The central carbon is quite negative, and both the C—C and $C\equiv S$ bonds are thus quite polar. As previously proposed,[1] the molecule has some ylidic character (**1a**). The calculated dipole moment is 1.21 D, which is half that of the previously calculated value.[2] The electronic properties discussed above show essentially no variation upon bending the CCS bond angle by 8.4°. For example, the degeneracy of the HOMOs is broken by only 0.01 eV in the C_s structure.

The charges on the fluorines in the CF_3 group are typical of those found in fluorocarbons, which usually fall in the range of 0.15–0.18 e with our basis set.[3,24] For example, $q(F) = -0.15$ e in CF_4. The charge distribution also argues against the presence of negative hyperconjugation in $CF_3C\equiv SF_3$.

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Note Added in Proof. In order to approximately account for correlation corrections, MP2 calculations (GRADSCF on a CRAY-1A) with the [6s4p1d/4s2p1d/4s2p] basis set including all valence electrons were performed at the optimum geometries for θ(CCS) = 180° and 171.6°. The geometric parameters from $\theta = 171.6°$ were used to generate structures with $\theta = 161.6°$ and 151.6°, and MP2 calculations also were done at these two geometries. (Each point required 8200 s of CPU time.) The lowest energy is found for $\theta = 171.6°$, and the energy for $\theta = 180°$ is 0.10 kcal/mol higher in energy. Compared to the energy for $\theta = 171.6°$, the energy for $\theta = 161.6°$ is 0.53 kcal/mol higher and for $\theta = 151.6°$ it is 1.70 kcal/mol higher. The minumum thus lies between $\theta = 170°$ and 180° at the MP2 level. Without complete geometry optimization with a correlated wave function, we cannot distinguish whether the molecule is linear or slightly bent considering the very small energy difference of only 100 cal/mol. Clearly the molecule is not bent significantly, and the MP2 results are consistent with our discussion and the experimental X-ray crystal structure.

Chiroptical Properties of Planar Acyclic 1,3-Dienes and α,β-Unsaturated Aldehydes: The Planar Diene Rule[1]

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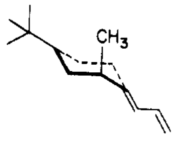
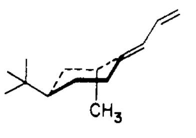
Abstract: The "planar diene rule" has been modified. The CD spectral results obtained with, inter alia, (*S*)-(+)-2,2,4,6,6-pentamethylcyclohexylideneacetaldehyde, (*S*)-(+)-2,2,4,6,6-pentamethylcyclohexylidenylpropene, (*S*)-(+)-(4-hydroxy-2,2,6,6-tetramethylcyclohexylidenyl)propene, and (*S*)-(+)-4-(*tert*-butyldimethylsiloxy)-2,2,6,6-tetramethylcyclohexylideneacetaldehyde are consistent with the hypothesis that a C–C bond is more dominant than a C–H bond and that a CH_3 group is more dominant than a ring CH_2. The absolute configuration, geometry, and conformations of a series of hindered 2,2,6,6-tetramethylcyclohexylidene derivatives of acetic acid, acetone, and acetaldehyde are discussed. X-ray structure of 4-hydroxy-2,2,6,6-tetramethylcyclohexylideneacetic acid is presented.

Examination of the long-wavelength $\pi-\pi^*$ Cotton effects of a large number of chiral acyclic planar 1,3-dienes and α,β-unsaturated aldehydes of known absolute configuration led to the formation of a "planar diene rule"[2] (Figure 1). This rule states that "after the 1,3-diene or α,β-unsaturated aldehyde chromophore and all the atoms attached to it are placed in a single plane, *oriented as shown in the diagram* (Figure 1), atoms or groups of atoms falling above the plane will make a positive contribution and those falling below the plane will make a negative contribution to the Cotton effect for the long-wavelength $\pi-\pi^*$ transition".

As applied to (*R*)-(+)-**1** (Figure 1), the chromophore is placed in the plane *as shown*, and one notes that the plane not only contains the four carbon atoms of the diene but also carbon atoms 2 and 6 of the cyclohexane ring and their attached equatorial hydrogen atoms.[2] Those atoms or groups of atoms lying in the plane will make very little, if any, contribution to the long-wavelength $\pi-\pi^*$ Cotton effect. The other atoms or groups of atoms closest to the chromophore[3] will determine the sign of the Cotton effect. Those found above the chromophore plane will make a positive contribution and those below a negative one, so that in (*R*)-(+)-**1** one notes that the allylic axial methylenes (ring CH_2) C_3 and C_5 as well as C_4 fall in the (+) space, whereas the allylic hydrogens H_A and H_B fall in the (–) space. This observation is consistent with the hypothesis[2,3] that a C–C bond is more dominant than a C–H bond in their respective contributions to the chiroptical properties of a molecule. It was also concluded, based on the Cotton effect observed for (*E*,2*S*,4*R*)-(+)-(2-methyl-4-*tert*-butylcyclohexylidenyl)propene (**2**) and (*Z*,2*S*,4*R*)-(+)-(2-methyl-4-*tert*-butylcyclohexylidenyl)propene (**3**) that an axial ring CH_2 group is more dominant than an axial methyl group.[2] However, this can be misleading since in these molecules one is really comparing *one* axial methyl with *two* ring CH_2 groups. The intent of this article is to clarify this point.



(*E*, 2*S*, 4*R*)-(+)-2



(*Z*, 2*S*, 4*R*)-(+)-3

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