electrons and is measured in units of energy. When a bond is formed between two neutral atoms the valence electrons move from the atom with the smaller electronegativity (the cation) toward the atom with the larger electronegativity (the anion). The difference in the free-atom electronegativities of the atoms entering into the bond thus indicates the direction and extent of the electron transfer and gives a measure of the ionicity of the resulting bond.

The concept of the Lewis acid strength as defined by eq 4 can also be traced back to Pauling.[3] It is an estimate of the valence of a typical bond formed by a cation and is given in valence units (electron pairs per bond). As suggested by its name, it is, in contrast to the electronegativity, intrinsically an ionic property since eq 4 (or eq 2) has no meaning for a free atom. Furthermore, again in contrast to the electronegativity, it can only be defined in terms of the strengths of bonds to a reference anion, here chosen to be O^{2-} because of the large amount of information available on the coordination of cations by O. In this model the species that enter into a bond are the ions rather than the free atoms, and during bond formation the electrons move from the anion to the cation, i.e. in the opposite direction to that implied by the free atom model. The extent of the transfer is given by Sa and Sb which are both estimates of the strength of the resulting bond.

The models underlying electronegativity and Lewis acid strength are therefore quite different, but the scales correlate because both depend on the nuclear charge screened by the core electrons (approximately equal to the formal oxidation state (V)) and the radius of the valence shell (approximately equal to the radius of the core electrons that form the surface of the cation (r)).

The Lewis acid strength and the spectroscopic electronegativity are conceptually quite distinct properties that correlate only because both reflect the properties of the surface of the electron core of an atom. While correlations like that given by eq 3 may be useful, one should not confuse two scales that derive from fundamentally different concepts. To avoid confusion, the term electronegativity should be reserved for those scales that are directly measured in units of energy. Others scales, like that of Boyd and Edgecombe,[8] constructed from surface properties other than energy, should be considered as scales that measure different properties but that correlate with the electronegativity for the reasons given above. Since the chemical properties of an atom are the properties of its surface, correlation between chemically useful scales that depend on these properties is not unexpected.

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Chiroptical Properties of the Diazirine Chromophore

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Abstract: Chiroptical properties of the diazirine chromophore are investigated experimentally and by ab initio molecular orbital calculations. Measurement of the CD spectra of (αS)-3-*sec*-butyldiazirine (**1**), (5*S*)-5-methyl-1,2-diazaspiro[2.5]oct-1-ene (**2**), (4*R*,7*R*)-4-isopropyl-7-methyl-1,2-diazaspiro[2.5]oct-1-ene (**3**), 3-azi-5α-cholestane (**4**), and 3-azi-5α-androstan-17β-yl benzoate (**5**) and computations on *gauche*-3-ethyldiazirine (**6**) suggest that the Cotton effect of the long wavelength (350-370 nm) absorption obeys an octant rule. The signs of the octants are the same as observed for the analogous carbonyl compounds. The octant nature of the sector rule is consistent with the nodal properties of the molecular orbitals in the description of the lowest excited state, $n_{-}\pi_{NN}^*$. It is anticipated that the octant rule for diazirines will prove applicable and useful in compounds containing other chromophores and in compounds containing a less strained cis-azo group.

The introduction of chromophore groups into a strained three-membered ring raises their stereochemical rigidity and, at the same time, practically has no effect on the nature of the lower electronic transitions. This, for example, was demonstrated in studying the halogenamino chromophore in a series of aziridines, diaziridines,[2] and oxaziridines.[3] The compounds containing stereochemically rigid chromophore groups are most suitable for developing the regional rules that correlate the Cotton effect (CE) sign with the stereochemistry of the chromophore environment. Therefore it is interesting to consider the diazirine chromophore as a rigid model of the cis-azo chromophore. The latter has been quite thoroughly investigated by CD and ORD methods.[4-6] However, the general regional rule for this chromophore has not been developed yet. The Snatzke empirical rule known so far[4] is applicable only to α-carbonyl-substituted pyrazolines.

The diazirine ring itself can be considered a prospective chromophore for studying the stereochemistry of chiral molecules by chiroptical methods since, in our opinion, this chromophore exhibits the following advantages: (i) high C_{2v} symmetry similar to the carbonyl chromophore; (ii) long-wavelength UV absorption (350-370 nm);[7,8] (iii) ready availability.[9,10] However, there are no studies of the chiroptical properties of this class of three-

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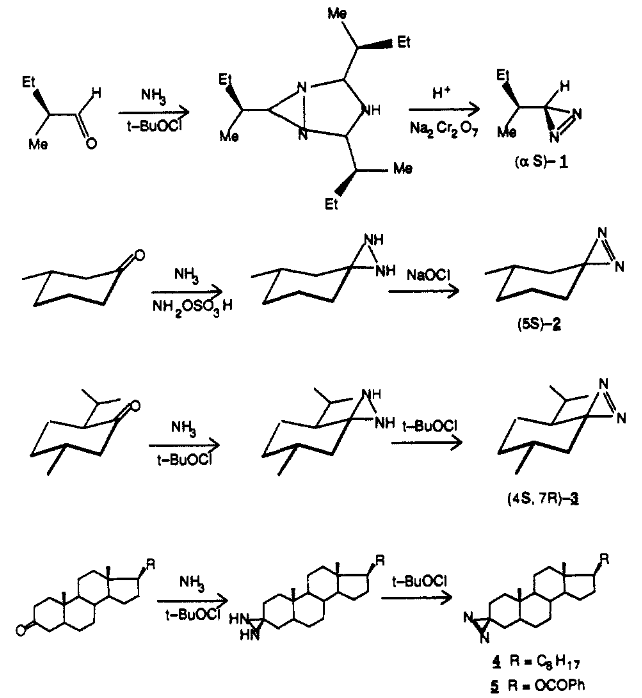
Scheme I



membered heterocycles despite the fact that a few optically active diazirines (based on steroids) have been previously described.[11]

To investigate the chiroptical properties of the diazirine chromophore, new optically active diazirines **1**–**5** (Scheme I) are synthesized, their CD spectra have been studied, and an ab initio quantum chemical study of the oscillator and optical rotatory strengths of the lower electronic transitions of a model system, 3-ethyldiazirine (**6**), in a chiral gauche conformation has been carried out.

Theoretical Method

The geometry of P-*gauche*-3-ethyldiazirine (**6**) was fully optimized by Hartree-Fock SCF calculations at the 6-31G level by using the GAUSSIAN 86 system of programs.[12] For the purpose of determining the transition properties, the wave functions were redetermined in center-of-mass coordinates and the addition of diffuse s and p functions to the basis sets of the C and N atoms, $\alpha_C = 0.020$ and $\alpha_N = 0.028$. Addition of the diffuse functions is required to describe the lowest few Rydberg states.

The method used to calculated oscillator and optical rotatory strengths is the same as was used previously[2,3] and has been described in detail elsewhere.[13] Partially correlated wave functions for the ground and excited states are determined to first order in Rayleigh–Schrodinger perturbation theory

$$\Psi_n = \Psi_n^o - \sum_j a_{nj}\Phi_j^o \qquad (1)$$

where

$$a_{nj} = \langle\Psi_n^o|H|\Phi_j^o\rangle / (\langle\Phi_j^o|H|\Phi_j^o\rangle - \langle\Psi_n^o|H|\Psi_n^o\rangle) \qquad (2)$$

H is the exact Hamiltonian, Φ_j^o is a singlet singly or more highly excited configuration derived from the Hartree–Fock determinant, Φ_{HF}, and Ψ_n^o is a linear combination of strongly interacting Φ_l^o ($l \neq j$) selected from at most singly excited configurations. Thus, for the ground state, $\Psi_o^o = \Phi_{HF}$. All configurations for which the interaction coefficient a_{nj} (eq 2) was greater than 0.03 were included in the zero-order part of the CI wave function.

Electric dipole transition moments in the length $\langle r\rangle_{on}$ and velocity $\langle\nu\rangle_{on}$ formalism and magnetic dipole transition moments $\langle m\rangle_{on}$ are explicitly evaluated from

$$\langle r\rangle_{on} = \langle\Psi_o|\mu|\Psi_n\rangle \qquad (3)$$

$$\langle\nu\rangle_{on} = \langle\Psi_o|\nabla|\Psi_n\rangle / (E_n - E_o) \qquad (4)$$

$$\langle m\rangle_{no} = -i\langle\Psi_n|m|\Psi_o\rangle \qquad (5)$$

where the operators μ, ∇, and m have their usual definitions[13] and

$$E_n = \langle\Psi_n|H|\Psi_n\rangle \qquad (6)$$

Oscillator strengths f_{on} are calculated by the "mixed" formalism

$$f_{on} = \tfrac{2}{3}\langle\Psi_o|\nabla|\Psi_n\rangle\cdot\langle r\rangle_{no} \qquad (7)$$

Optical rotatory strengths are evaluated as

$$[R_{on}]^r = \langle r\rangle_{on}\cdot\langle m\rangle_{no} \qquad (8)$$

and in the origin-independent form

$$[R_{on}]^\nu = \langle\nu\rangle_{on}\cdot\langle m\rangle_{no} \qquad (9)$$

The extent of the deviation of $\langle r\rangle$ and $\langle\nu\rangle$ from collinearity and in magnitude is a measure of the quality of the wave function for the particular states and of the origin dependence of $[R]^r$. The objective of the above procedure is to obtain electric and magnetic dipole transition moments correct to first order in electron correlation, as is also the case for CD calculations based on the RPA approximation.[14]

Experimental Section

The CD spectra were measured on a JASCO J-500A spectropolarimeter with a DP-500N data processor, the UV spectra on a Specord UV–vis spectrophotometer, the ^{1}H NMR spectra on a Bruker WM-400 spectrometer (400 MHz, from TMS), and the optical rotation angles on a Polamat A polarimeter.

(*αS*)-3-*sec*-Butyldiazirine (1). Upon cooling (−50 °C) and stirring, a solution of *t*-BuOCl (2.26 g, 21 mmol) in *t*-BuOH (3 mL) and (*S*)-2-methylbutanal ($[\alpha]^{20}{}_D$ +28.5°, neat[15]) (3.45 g, 40 mmol) were added dropwise to absolute methanol (25 mL) saturated with dry NH$_3$ at 20 °C. After having been stirred for 1 h at 20 °C, the solvent was evaporated in vacuo and the product was extracted from residue with absolute ether. After removal of ether, 2.13 g (63%) of **2,4,6-tri-*sec*-butyl-1,3,5-triazabicyclo[3.1.0]hexane** (TABH), mp 91–117 °C, $[\alpha]^{20}{}_D$ +14.1° (*c* 2.5 hexane) was obtained. Anal. Found: C, 71.2; H, 12.5; N, 16.5. Calcd for $C_{15}H_{31}N_3$: C, 71.1; H, 12.3; N, 16.6. A solution of **TABH** (0.38 g, 1.5 mmol) in d_{12}-cyclohexane (2 mL) was stirred for 1 h at 70 °C, with a solution of $Na_2Cr_2O_7 \cdot 2H_2O$ (1.34 g, 4.5 mmol) in 2 N H_2SO_4 (10 mL). The organic layer was separated, washed sequentially with water, 10% aqueous NH_2OSO_3H, water, 20% aqueous solution of KOH, and water and dried over K_2CO_3. A d_{12}-cyclohexane (1.8 mL) containing 0.069 g (47%) of diazirine **1** was obtained. The aliquot of this solution was taken and diluted with the corresponding solvent to measure the optical rotation angle, the CD, and ^{1}H NMR spectra. $[\alpha]^{20}{}_D$ +28.8° (*c* 0.6 in hexane). ^{1}H NMR in d_{12}-cyclohexane (*J*, Hz): δ 0.5 (3-H, ^3J = 4.6), 0.79 (*Me*CH, ^3J = 6.8), 0.97 (*Me*CH$_2$, ^3J = 7.3), 0.99 (CH), 1.18 and 1.33 ppm (CH$_A$H$_B$, J_{AB} = 14.5).

(5*S*)-5-Methyl-1,2-diazaspiro[2.5]oct-1-ene (2) was obtained from (3*S*)-3-methylcyclohexanone ($[\alpha]^{20}{}_D$ −13.0°, neat) according to the procedure described for racemate **2**,[3] yield 25%, bp 45 °C (30 mm), $[\alpha]^{20}{}_D$ +13.4° (*c* 1, heptane).

(4*S*,7*R*)-4-Isopropyl-7-methyl-1,2-diazaspiro[2.5]oct-1-ene (3). A solution of (−)-menthone (9.17 g, 59.5 mmol) in absolute CH$_2$Cl$_2$ (50 mL) was saturated with dry NH$_3$ for 2 h. A solution of *t*-BuOCl (6.5 g, 60 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise to the obtained solution with cooling (−40 °C) and stirring. After 10 h at 20 °C, the precipitate was filtered off, the solution was evaporated in vacuo, and the residue was dissolved in ether (50 mL). The product was extracted from the ether solution with a cold (5 °C) 10% aqueous solution of H$_2$SO$_4$ (5 × 20 mL). The acid solution was washed with ether and neutralized with

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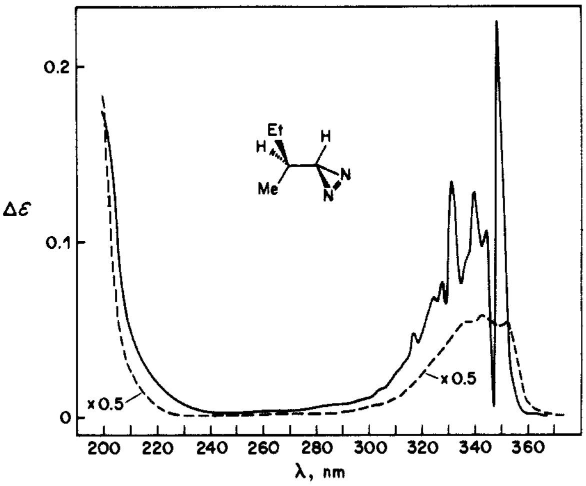


Figure 1. The CD spectra of diazirine **1** in heptane (—) and in MeOH (---).

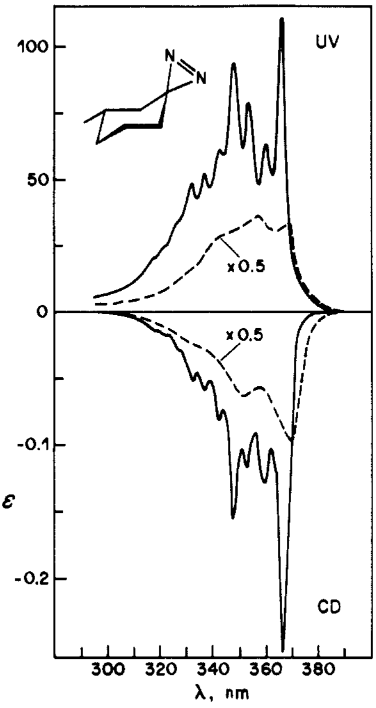


Figure 2. The UV and CD spectra of diazirine **2** in heptane (—) and in MeOH (---).

40% aqueous solution of KOH upon cooling (5–10 °C). The cold solution was saturated with KOH pellets and the product extracted with ether and dried over K_2CO_3. After removal of ether, the residue was sublimated at 20 °C (1 mm), providing 0.7 g (7%) of **(4*S*,7*R*)-4-isopropyl-7-methyl-1,2-diazaspiro[2.5]octane** (DASO), mp ~30 °C, $[\alpha]^{20}{}_D$ −41.7° (*c* 3.2, hexane). Anal. Found: C, 71.5; H, 12.2; N, 16.5. Calcd for $C_{10}H_{20}N_2$: C, 71.4; H, 12.0; N, 16.65. A solution of *t*-BuOCl (0.13 g, 1.2 mmol) in absolute ether (3 mL) was added to a solution of DASO (0.125 g, 0.74 mmol) in ether (3 mL) with cooling (−70 °C) and stirring. After solvent removal, the residue was distilled in vacuo, providing diazirine **3** (0.092 g, 74%), bp 98 °C (17 mm), $[\alpha]^{20}{}_D$ −9.2° (*c* 1.1, hexane). Anal. Found: C, 72.5; H, 11.0; N, 16.7. Calcd for $C_{10}H_{18}N_2$: C, 72.2; H, 10.9; N, 16.85. ^{1}H NMR in $CDCl_3$ (J, Hz): δ 0.45 (8-H_e, $^2J = 13.9$, $^3J_{ea} = 4.3$, $^3J_{ee} = 2.0$), 0.54 and 0.71 (Me_2C, strongly coupled system), 0.71 (MeC*H*), 0.87 (7-Me, $^3J = 6.8$), 1.02 (6-H_a, $^2J = 11.5$, $^3J_{aa} = 12.5$, $^3J_{ea} = 3.2$), 1.38 (5-H_a, $^2J = {}^3J_{aa} = 12.5$, $^3J_{ea} = 3.2$), 1.40 (8-H_a, $^3J_{aa} = 12.2$), 1.53 (4-H_a, $^3J = 4.6$, $^3J_{ea} = 3.7$), 1.78 (5-H_e, $^3J_{ea} = 3.7$, $^3J_{ee} = 2.0$), 1.78 (7-H_a, $^3J_{ea} = 3.7$), 1.86 ppm (6-H_e).

3-Azi-5α-cholestane (4). A solution of 5α-cholestan-3-one (0.97 g, 2.5 mmol) in absolute CH_2Cl_2 (50 mL) was saturated with dry NH_3 for 2 h. A solution of *t*-BuOCl (1.3 g, 12.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise to the obtained solution with cooling (−40 °C) and stirring. After 48 h at 20 °C, the reaction mixture was washed with water and dried over $MgSO_4$. After removal of the solvent, the residue (0.95 g) containing crude **3,3-hydrazo-5α-cholestane** was dissolved in absolute ether (50 mL). A solution of *t*-BuOH (0.31 g, 2.8 mmol) in ether (5 mL) was added dropwise to the obtained solution with cooling (−60 °C) and stirring. After the solvent removal, the residue was recrystallized from EtOH, providing 0.94 g (93%) of diazirine **4**, mp 91–92 °C, $[\alpha]^{20}{}_D$ +37.5° (*c* 0.8 $CHCl_3$). Anal. Found: C, 81.1; H, 11.7; N, 6.9. Calcd for $C_{27}H_{46}N_2$: C, 81.3; H, 11.6; N, 7.0. ^{1}H NMR in $CDCl_3$ (J, Hz): δ 0.10 (4-H_e, $^2J = 14.3$, $^3J_{ea} = 3.9$, $^3J_{ee} = 2.2$), 0.33 (2-H_e, $^2J = 14.7$, $^3J_{ea} = 4.8$, $^3J_{ee} = 2.2$), 0.66 (13-Me), 0.85 and 0.86 (Me_2C, $^3J = 6.8$), 0.87 (10-Me), 0.90 (*Me*CH, $^3J = 6.6$), 1.77 (4-H_a, $^3J_{aa} = 13.0$), 1.97 (2-H_a, $^3J_{aa} = 13.6$, $^3J_{ea} = 4.8$), 0.65–2.01 ppm (others).

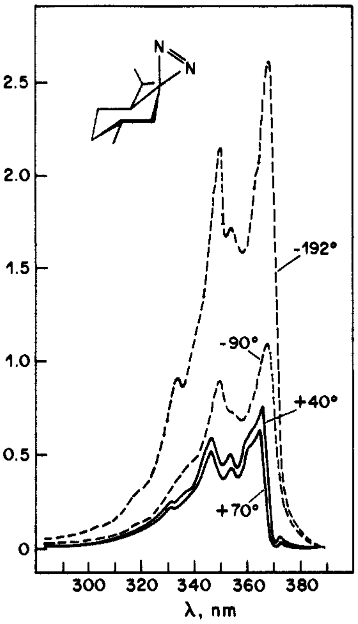


Figure 3. The CD spectra of diazirine **3** in heptane (—) and in EPA (---) at different temperatures.

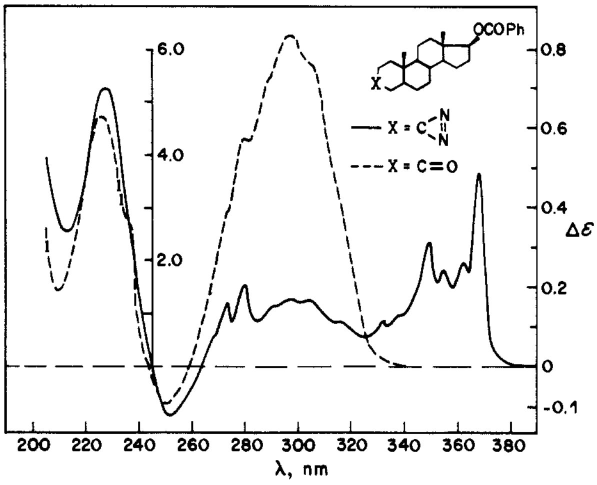


Figure 4. The CD spectra of diazirine **5** and the corresponding ketone in heptane.

3-Azi-5α-androstan-17β-yl benzoate (5) was obtained from 3-oxo-5α-androstan-17β-yl benzoate as described above. Yield 90%, mp 145–146 °C (from EtOH–EtOAc), $[\alpha]^{20}{}_D$ +63.2° (*c* 1, $CHCl_3$). Anal. Found: C, 76.9; H, 8.2; N, 7.1. Calcd for $C_{26}H_{34}N_2O_2$: C, 76.8; H, 8.4; N, 6.9. ^{1}H NMR in $CDCl_3$ (J, Hz): δ 0.13 (4-H_e, $^2J = 14.4$, $^3J_{ea} = 3.9$, $^3J_{ee} = 2.2$), 0.34 (2-H_e, $^2J = 14.8$, $^3J_{ea} = 5.0$, $^3J_{ee} = 2.2$), 0.9 (1-Me), 0.94 (13-Me), 1.79 (4-H_a, $^3J_{aa} = 13.1$), 1.99 (2-H_a, $^3J_{aa} = 13.8$, $^3J_{ea} = 5.0$), 4.85 (17-H_a, $^3J_{aa} = 9.2$, $^3J_{ea} = 7.8$), 7.44, 7.55, 8.04 (Ph), 0.8–2.3 ppm (others).

Results and Discussion

In the CD spectra of diazirines **1–5**, a dichroic absorption band is observed in the range 300–370 nm (Table I) which, similar to UV spectra, is well separated from the short-wavelength absorption and exhibits a fine structure (Figures 1–4). In polar protic solvent MeOH, this structure practically disappears (Figure 1, 2) and

Table I. Chiroptical Properties of Diazirines **1–5**

compd	solvent		UV and CD maxima: λ, nm (ε or Δε ×100)								
1	CD	heptane	350 (+22)	345 (+11)	340 (+12)	332 (+13)	328 (+8)	324 (+7)	318 (+5)	200 (+17)	
		MeOH	351 (+11)	343 (+12)		335 (+11)				200 (+37)	
	UV	heptane	347 (211)	344 (154)	337 (170)	330 (176)		322 (114)	316 (87)		
		MeOH	348 (145)		339 (153)	333 (158)					
2	CD	heptane	367 (−25)	360 (−13)	353 (−12)	348 (−16)		336 (−6)	332 (−5)	321 (−2)	317 (−1.4)
		MeOH	369 (−16)			346 (−13)			327 (−5)		
	UV	heptane	366 (110)	360 (63)	353 (78)	348 (93)	342 (61)	336 (52)	331 (48)	321 (23)	317 (19)
		MeOH	369 (64)		352 (72)		339 (47)				
3	CD	heptane	372 (+4)	365 (+81)	361 (+63)	354 (+51)	347 (+63)	331 (+26)	317^a (+8)	200 (+59)	
		MeOH		367 (+65)			350 (+56)	335 (+27)	320 (+9)	197 (+55)	
	UV	heptane		365 (103)	360^a (89)	352^a (97)	347 (110)	331^a (59)	317^a (20)		
		MeOH		365 (65)			349 (77)	334^a (47)	320^a (21)		
4	CD	heptane	369 (+43)	363 (+23)	356 (+22)	350 (+28)	345^a (+16)	339 (+12)	333 (+10)	319 (+4)	205 (+138)
		MeOH	371 (+31)		353 (+26)			338 (+12)			208 (+104)
	UV	heptane	368 (100)	362 (55)	355 (72)	349 (83)	344^a (56)	338 (49)	333 (44)	323 (24)	318 (21)
		MeOH	370 (56)		352 (62)			339^a (40)			
$\mathbf{5}^b$	CD	heptane	369 (+47)	363 (+25)	356 (+24)	350 (+31)		339 (+12)	333 (+12)		
		MeOH	371 (+36)		353 (+30)			338 (+15)			
	UV	heptane	368 (120)	362 (66)	355 (86)	349 (100)	344 (66)	337 (58)	332 (52)	327 (34)	322 (28)
		MeOH	370 (72)		352 (80)			339^a (52)			

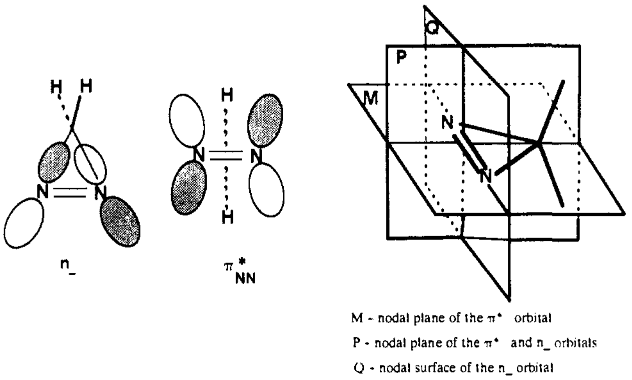
[a] Shoulder. [b] Dichroic absorption bands of benzoate chromophore λ_{max}, nm (Δε ×100): 298 (+16), 280 (+21), 273 (+16), 252 (−12), 228 (+527) in heptane; 280 (+33), 274 (+30), 229 (+558) in MeOH.

Table II. Electronic States and Transition Properties for P-*gauche*-3-Ethyldiazirine (**6**)[a]

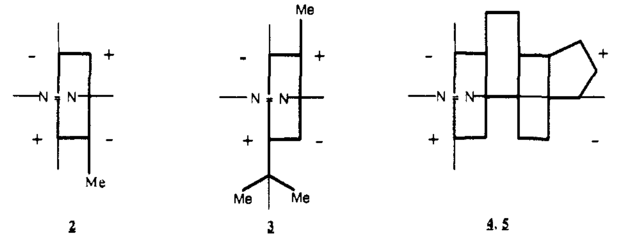
state	description	$[R]^{r\,b}$	$[R]^{v\,b}$	f	ΔE, eV	$\langle r^2\rangle^c$
1	MO 19 → π_{NN}^* ($n_- \rightarrow \pi_{NN}^*$)[d]	+4.08	+4.20	0.0168	3.82	13.5
2	MO 19 → 3p, σ^*_{CH}	−1.70	−2.04	0.0021	8.01	64.2
3	MO 19 → 3p	−0.71	−0.74	0.0152	8.46	69.4
4	MO 19 → 3p	+12.96	+12.71	0.0210	8.50	69.7
5	MO 19 → ?	−16.08	−13.43	0.025	8.63	74.9

[a] 6-31G optimized geometry, E(SCF) = −225.761 396 hartrees; properties in this table calculated with 6-31G + diffuse s,p basis (see text), E(SCF) = −225.765 006 hartrees. [b] 10^{40} cgs. [c] Average size of "upper" orbital in units of bohr^2. [d] The orbitals n_- and π_{NN}^* are shown in Figure 5.

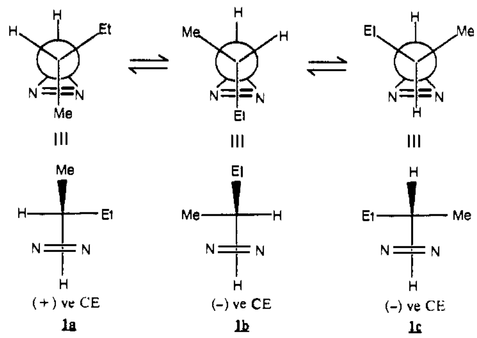
Scheme II



Scheme III



Scheme IV



similar to the case of UV spectra (Table I, Figure 2),[7] a slight red shift of the longest wavelength peak is observed. It is interesting to note that the long wavelength CE of diazirines **1–5** coincides in sign with the nπ* transition of the respective carbonyl compounds, i.e., diazirine **1** and (*S*)-2-methylbutanal ($\Delta\epsilon_{302}$ +0.102 in heptane), diazirine **2** and (*S*)-3-methylcyclohexanone,[16] diazirine **3** and (2*S*,5*R*)-menthone,[17] diazirine **4** and 5α-cholestan-3-one,[18] and diazirine **5** and 3-oxo-5α-androstan-17β-yl benzoate.[19]

The 6-31G structure of P-*gauche*-3-ethyldiazirine (**6**) is shown in Figure 5. The calculated excitation energies and oscillator and optical rotatory strengths for the five lowest electronic transitions are listed in Table II. The calculations indicate that the lowest electronic transition is a transition to a valence state and is well separated from the next few transitions to Rydberg states. The calculated excitation energy, 3.82 eV (≡324 nm), falls in the range of the experimentally observed absorption bands for **1–5**. The orbitals involved in the transition are shown in Figure 5. The transition originates from the HOMO, designated n_-, the out-of-phase combination of the nonbonded electron pairs on each N, which forms one of the Walsh-like bonding orbitals of the three-membered ring. This orbital also extends into the ring substituent group. The terminal orbital of the transition is the π* orbital of the NN bond, π_{NN}^*. The nature of the lowest energy electronic transition in the parent diazirine has been discussed on a number of occasions.[20-22] The $n_-\pi_{NN}^*$ transition is weakly

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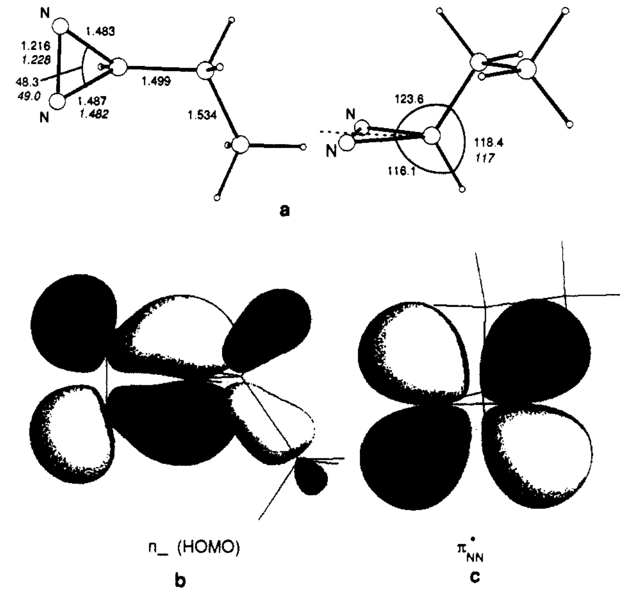
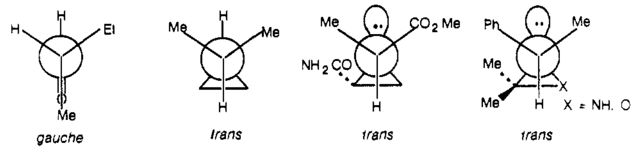


Figure 5. (a) The 6-31G structure of P-*gauche*-3-ethyldiazirine (**6**) (distances in Å, angles in deg) with the equivalent experimental values for diazirine in italics (ref 27). (b, c) The orbitals involved in the $n_-\pi_{NN}^*$ transition, 0.05 contour. The nodal surface containing the N=N bond in the HOMO (b) suggests octant, rather than quadrant behavior of the HOMO–LUMO transition.

Scheme V



electric-dipole allowed in the parent diazirine and is also calculated to be weakly allowed in **6** ($f = 0.0168$). The conformation with P-chirality shown in Figure 5 is predicted to have a moderately large positive rotatory strength for the $n_-\pi_{NN}^*$ transition.

Due to the nodal structure of the orbitals participating in the $n_-\pi_{NN}^*$ transition (Figure 5 and Scheme II), an octant rule can be suggested for the diazirine chromophore. The distribution of signs of back octants is determined by the known absolute configurations of the chiral centers in diazirines **2–5** (Scheme III) and the computed results for **6**. For compounds **2** and **3**, the more highly populated conformation with equatorial orientation of the substituents is considered. It was confirmed by the ^{1}H NMR spectra on the basis of spin coupling constants $^3J = {}^3J(4a,5a) = 11.3$ Hz, $^3J(4e,5a) = 3.9$ Hz for diazirine **2**;[3] $^3J(4a,5a) = {}^3J(6a,7a) = 12.5$ Hz, $^3J(4a,5e) = {}^3J(6e,7a) = 3.7$ Hz for diazirine **3**.

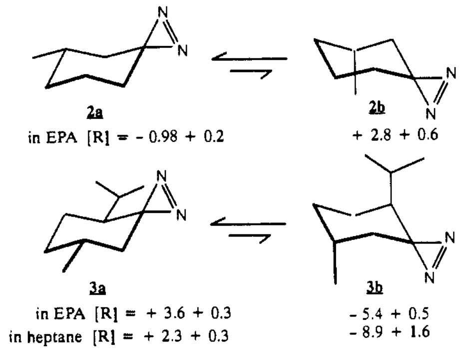
In the case of diazirine **1** having a positive CE (Figure 1) the octant rule predicts a noticeable population of rotamer **1a** with the gauche orientation of vicinal protons and eclipsing of the methyl group by the ring. Two other possible rotamers, *gauche*-**1b** and *trans*-**1c**, should exhibit negative and weak negative CE, respectively, according to the octant rule. An increase of the positive CE of diazirine **1** solution in EPA to −192 °C (Table II) suggests the thermodynamic preference of rotamer **1a**, at least relative to **1b**. Additionally, in terms of the relative population of trans and gauche rotamers, it may be that diazirines are similar to carbonyl compounds for which gauche rotamers are more advantageous (see, for example, (*S*)-2-methylbutanal[23]), while in saturated three-membered rings, trans rotamers are populated predominantly (see, for example, cyclopropanes,[24] aziridines, diaziridines, and oxaziridines[25]). When cooled in EPA to −192 °C, diazirines **2** and **3** exhibit an increase in the optical rotatory strength of the $n_-\pi^*_{NN}$ transition similar to their carbonyl analogues, (*S*)-3-methylcyclohexanone[16] and (2*S*,5*R*)-methone.[17] Evidently the population of the most stable conformers with the equatorial orientation of the substituents increases in these cases. In accordance with the proposed rule, axial conformers are supposed to exhibit the opposite contribution to the CE, namely positive for diazirine **2** and negative for diazirine **3**. Heating diazirine **3** in heptane solution results in a decrease of CE. However, in contrast to 1-menthone, the long-wavelength dichroic absorbance band exhibits no shift into the region of negative values for $\Delta\epsilon$ (Figure 3). The rotatory strengths $[R_a]$ and $[R_b]$ and the ratio of equatorial and axial conformers **a**/**b** can be evaluated from the linear dependence of the observed rotatory strength $[R_0^T]$ on $1/(1 + \exp(-\Delta G°/NkT))$ on the assumption that $\Delta S° = 0$[26] (Table III).

Table III. The Temperature Dependence of the Optical Rotatory Strength of the $n_-\pi^*$ Transition of Diazirines **1–3**

1	**2**		**3**		
$[R_0^T]^a$	$[R_0^T]$	$(\mathbf{a}/\mathbf{b})^b$	$[R_0^T]$	$(\mathbf{a}/\mathbf{b})^b$	T, K
2.605	−1.071	99.8:0.2	3.252	98.3:1.7	81
1.050	−0.836	96.4:3.6	2.640	89.5:10.5	153
0.777	−0.769	93.9:6.1	2.289	85.7:14.3	183
0.559^c	−0.633	91.3:8.7	2.012	82.3:17.3	213
0.387	−0.534	88.7:11.3	1.724	79.4:20.6	243
0.307	−0.488	86.2:13.8	1.449	76.8:23.2	273
0.214	−0.375	84.7:15.3	1.373	75.3:24.7	293
			1.555	93.2:6.8	298
			1.473	92.4:7.6	313
			1.407^d	91.8:8.2	323
			1.325	91.2:8.8	333
			1.282	90.7:9.3	343

^{a} $[R_0^T] \approx (1.08 \times 10^{40})R_0^T$ (CGSE). ^{b} The ratio of equatorial and axial isomers. ^{c} In EPA. ^{d} In heptane.

Scheme VI



The decreasing **a**/**b** ratio for diazirine **3** as compared to diazirine **2** in EPA appears to be due to steric repulsion between the equatorial isopropyl group and the diazirine ring. Destabilization of equatorial isomer **3a** is also promoted by solvation of the diazirine ring by polar solvent, which is seen from comparison of the ratio **3a**/**3b** in EPA and heptane (Table III). Djerassi et al.[17] evaluate the ratio of the equatorial and axial conformers of 1-menthone as 97:3 (EPA, 25 °C). Consequently the gauche rotamers of diazirines (corresponding to the equatorial conformer) are not so advantageous in the case of carbonyl compounds. Thus we can conclude that in terms of the ratio of gauche and trans rotamers, diazirines hold an intermediate position between car-

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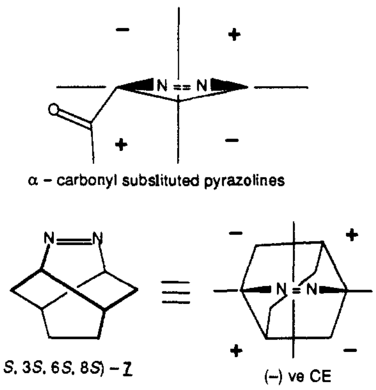
Scheme VII



bonyl compounds and saturated three-membered rings.

Owing to the fact that the $n_-\pi^*$ transition band of the diazirine chromophore is located in the long-wavelength range of the CD spectrum, this chromophore can be employed for studying the stereochemistry of compounds containing additional chromophores with absorption maxima less than 300 nm: >C=O, $-N_3$, >C=N–, Ar, and others. For example, in the CD spectrum of diazirine **5**, the $n_-\pi^*$ transition of the diazirine chromophore is well separated from the $1L_b$ transition of the benzoate group, while in the case of 3-oxo-5α-androstan-17β-yl benzoate, overlapping of the absorption bands of the carbonyl and benzoate chromophores is observed (Figure 4).

The octant rule found for diazirines is certain to be applied in the case of the compounds containing a non-strained cis-azo group since the long-wavelength transition of both chromophores is of the same nature $(n_-\pi^*_{NN})$.[4] In fact, the above rule reliably predicts the sign of the long-wavelength band in the CD spectra of the known chiral cis-azo compounds. In the case of α-carbonyl-substituted pyrazolines,[4] the CE sign is mainly determined by the octant in which the carbonyl group enters. In the case of 4,5-diaza-twist-4-ene **7**[6] similar to its carbonyl analogue 9-twistbrendanone,[15] the decisive contribution to the CE is made by the closer "outer" rings. Thus the general regional rule for studying the stereochemistry of chiral cis-azo compounds is proposed on the basis of studying of chiroptical properties of the diazirine chromophore.

Organosilicon Rings: Structures and Strain Energies

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Abstract: Geometries, strain energies, and electronic structures for 23 organosilicon compounds have been determined. The species studied were those for which silicon successively replaced carbon in cyclopropane, bicyclobutane, and [1.1.1]propellane and in propane, cyclobutane, and bicyclo[1.1.1]pentane. Wave functions constructed from the recently developed compact effective core potentials and using a split-valence, d-polarized basis set were employed. Accurate strain energies, validated by extensive comparison with existing experimental data and ab initio calculations, were obtained from a series of homodesmic reactions. When the compounds investigated are displayed in a periodic table format (increasing number of silicon replacements down a column, increasing number of fused rings across rows) many useful interrelationships and bonding patterns manifest themselves. In spite of their considerable complexity in structure and properties, it proves possible to understand them in terms of electronegativity arguments and a simple two-orbital, three-atom, molecular orbital model. Our results also predict several interesting new organosilicon compounds, and an analysis of their synthetic accessibility suggests that these new species should be realizable.

Organosilicon chemistry is an exciting and rapidly growing field. Silicon compounds with Si_3 and Si_4 rings are now well represented in silicon chemistry[1] due in large part to recent intensive research on silicon double bonds and on silylenes.[2] Larger rings have also been studied extensively including cagelike species up to Si_9 and Si_{10}.[3] The advancements in these experimental studies have prompted considerable theoretical effort to understand Si–Si and Si–C double bonding.[4] A few theoretical studies on Si_3, Si_4, and Si_6 strained rings also have been undertaken.[5-8] Important results have been obtained, but it is not surprising that with these larger systems different levels of accuracy have made it difficult to discern trends and make comparisons.

In this work we present ab initio effective core potential electronic structure results[9] on silicon-containing strained rings generated from uniform basis sets using compact effective potentials to represent the core electrons. Results from these calculations are compared with experiment and with all-electron calculations and are found to provide accurate and consistent geometries and good estimates of strain energies. The efficiency of the recently developed compact effective core potentials employed here has enabled us to make comparisons with the well-known hydrocarbon literature[10-12] on strained ring systems and to extend our investigation to the corresponding mixed silicon–carbon ring systems and to the silanes. The large set of molecules treated has led to

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