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Substituent Effects on the Geometries and Energies of Cyclopropanes and the Corresponding 2-Propyl Derivatives

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Abstract: Ab initio (4-31G//4-31G) molecular orbital calculations on substituted cyclopropyl (C_3H_5X) and isopropyl (C_3H_7X) compounds, where X = Li, BeH, BH_2, CH_3, NH_2, OH, and F, enable both geometrical and energetic trends to be ascertained. Contrary to implications in the literature, many of these are not unique to cyclopropane but are found in the 2-propyl systems as well. The cyclopropyl group is more electronegative than 2-propyl; hence σ-donors stabilize the ring, whereas σ-acceptors are destabilizing. π-Acceptors do produce special stabilization and geometrical effects, but only very strong π-donors (NH_2 and O^-) are also able to stabilize cyclopropane. The origins and geometrical consequences of these effects are analyzed in terms of molecular orbital interactions.

Nearly a century ago, Baeyer[1] attributed the high reactivity of cyclopropane to the "stress"[2] or "strain" (Spannung) associated with the large deviation of the carbon valence angles from the ideal tetrahedral value. The unusual chemical, structural, and electronic properties of cyclopropane have intrigued chemists ever since.[3,4] Our concern, the nature of the interaction of cyclopropane with substituents, has both energetic and geometrical consequences. Many chemical processes involving cyclopropanes are strongly influenced by substituents (Figure 1). These include the displacement of norcaradiene–cycloheptatriene (**1**), bridged annulene (**2**), semibullvalene (**3**) and related equilibria,[5] rates of bicyclo[2.1.0]pentane ring openings (**4**),[6] and distal (C_2–C_3) vs. vicinal (C_1–C_2) orientations of hydrogenolysis (**5**)[7,8] and other ring C–C bond cleavages.[8] While discernible patterns appear to have emerged from studies on such relatively complicated systems, full understanding of cyclopropane substituent effects is far from having been achieved. Thus, Fuchs et al.[9] conclude that only cyclopropylbenzene shows appreciable thermochemical stabilization; relative to the corresponding 2-propyl derivatives, no significant effect is found for cyano (a good π-acceptor), amine (a good π-donor), and *gem*-dimethyl substituents. Furthermore, interactions between groups separated by a "saturated center", e.g., in the –XCH—CH═CH– moieties in Figure 1, can be quite appreciable and influence the equilibria.[10] The simplest systems afford the best bases for definitive studies.

A particularly dramatic example, the strong stabilization of the carbenium ion in cyclopropylcarbinyl cations,[11] has long been known and is well understood.[12] In the bisected conformation, one of the degenerate high-lying Walsh[13] cyclopropane HOMO's (3e′)[14] donates electrons to the substituent vacant p or π^* orbital. The C_1–C_2 (vicinal) bonds are lengthened and the C_2–C_3 (distal) bonds shortened in such situations.[11,12,14-16] In the perpendicular conformation, the C–C bond lengths are normal. Similar reasoning was applied by Hoffmann[15] and a little later by Günther[16] to explain the stabilization of norcaradiene forms by π-acceptor substituents.[5] These structural conclusions were consistent with X-ray,[17] microwave,[18] and ab initio studies on several cyclo-

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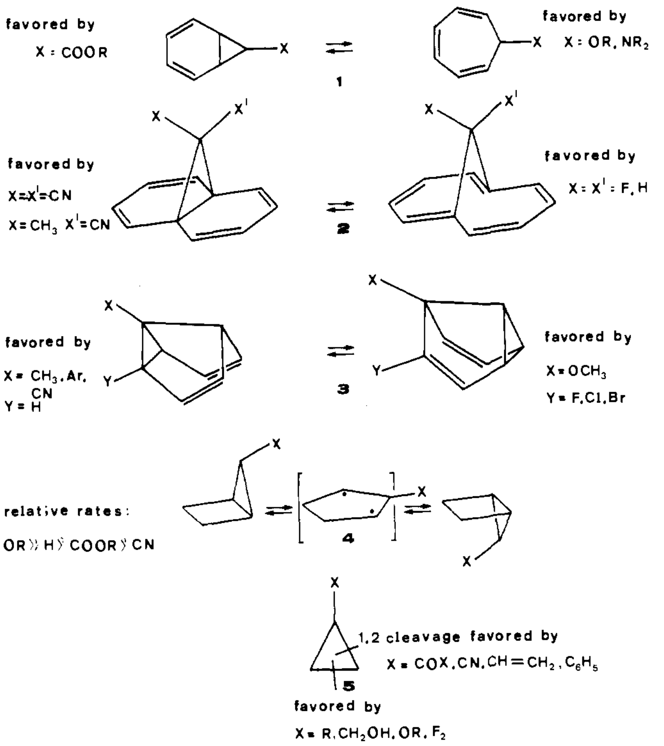

Figure 1. Examples of substituent effects in processes involving cyclopropane ring systems.

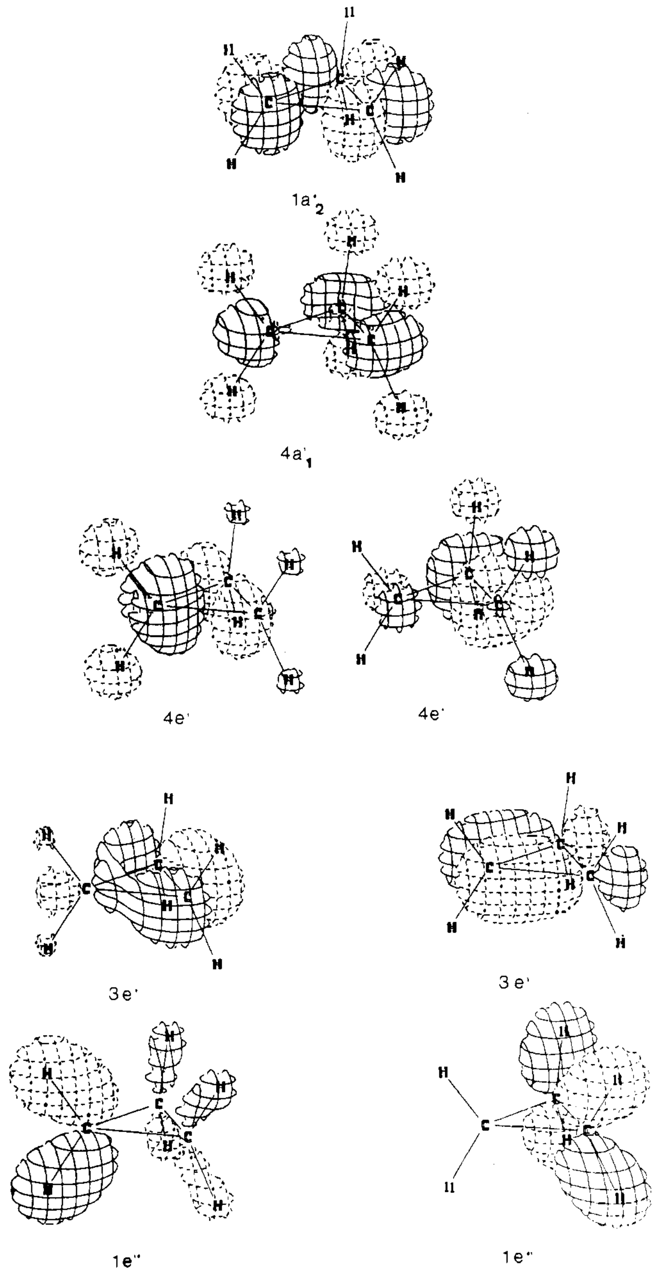

Figure 2. Jorgensen–Salem[14,42] plots of eight cyclopropane MO's using STO-3G wave functions. The six Walsh orbitals are shown at the top. All orientations have the substitution site, C$_1$, at the left. In the text, the degenerate MO's are differentiated by "L" (left) and "R" (right).

propanes with CN,[19,20] vinyl,[20] NO$_2$,[21] etc., substituents (Table I) and are now firmly established. The extensive literature has been reviewed by Allen.[17]

The situation with regard to "lone-pair" substituents[22] is less satisfactory. *gem*-Difluoro groups destabilize three-membered rings and facilitate the cleavage of distal bonds (Figure 1).[8,23] In 1970 both Hoffmann[15] and especially Günther[16] argued that π-donors, by interacting with the vacant Walsh orbital of 1a$_2'$ symmetry (II),[14] should lengthen *all* the cyclopropane C–C bonds (Figure 2). However, this prediction was shown experimentally *not* to be correct for 1,1-difluorocyclopropane[24] and, in the latest interpretation of microwave data, for cyclopropylamine.[25] Both have *shortened* vicinal bonds (see Table I); only the distal bonds are longer. The C–N rotational barrier in cyclopropylamine is quite small[26] (indicating little interaction with the ring), and less difference in the C–C bond lengths is found calculationally.[22,27] Further ab initio and microwave data on cyclopropanes with a number of substituents—F;[22-24] Cl and 1,1-Cl$_2$;[28] OH, O$^-$, OH$_2^+$, NH$_3^+$, and CH$_2^-$;[22] CH$_3$;[27,29] Li;[27] and SiH$_3$[30]—are summarized in Table I.

Durmaz and Kollmar[22] concluded that the influence of lone-pair substituents on the structures of cyclopropanes was due to "local effects such as changes in hybridization and steric interactions" rather than to the σ-acceptor or π-donor capabilities of the substituent. In other words, each system requires a special explanation.

In contrast to the extensive investigations of the effects of substituents on cyclopropane structures (Table I and ref 17), the

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Table I. Published Experimental and ab Initio C–C and C–X Bond Lengths (Å) of Substituted Cyclopropanes, C_3H_5X

substituent	method or basis set[a]	C_1–C_2 vicinal	C_2–C_3 distal	C–X	ref
none	ED	1.510 (2)	1.510 (2)		*b*
	Raman	1.512 (3)	1.512 (3)		*b*
	x-ray	1.509 (2)	1.509 (2)		17
	STO-3G	1.502	1.502		*c*
	3-21G	1.513	1.513		*c*
	4-31G	1.502	1.502		48
	6-31G*	1.498	1.498		*c*
F	DZ	1.497	1.528	1.391	*b*, 24c
1,1-F_2	MW	1.464 (2)	1.533 (1)	1.355 (2)	*b*, 24a
	STO-3G	1.511	1.518	1.368	32
	DZ	1.475	1.551	1.369	*b*, 24c
	4-31G	1.464	1.537	1.366	*d*
Cl	MW	1.513 (8)	1.515 (3)	1.740 (11)	50
	DZ	1.520	1.532	assumed	*b*, 28a
1,1-Cl_2	ED + MW	1.494 (3)	1.535 (9)	1.756 (2)	*b*, 28b
	MW	1.492	1.529	1.756	*b*, 28b
	4-21 + d on Cl	1.503	1.523	1.771	*b*, 28b
NH_2					
s-trans	MW	1.486 (8)	1.513 (3)	1.462 (13)	25
	DZ	1.508	1.512	1.451	27
	DZ	1.500	1.518		22
NH_3^+	DZ	1.500	1.514		22
CH_2^+					
bisected	STO-3G	1.609	1.454	1.384	11, 12
bisected	4-31G	1.664	1.412	1.347	12
perpendicular	STO-3G	1.512	1.513	1.480	11, 12
CH_2^-					
bisected	DZ	1.524	1.530		22
CN	MW	1.528 (5)	1.500 (2)		19
	4-21G	1.525	1.505	1.435	20a
NO_2					
bisected	4-21G	1.514	1.503	1.458	21
perpendicular	4-21G	1.497	1.522	1.475	21
$CH{=}CH_2$					
	ED	1.522	1.522	1.475	51
s-trans	4-21G	1.522	1.510	1.482	20a
s-cis	4-21G	1.522	1.508	1.491	20a
s-trans	3-21G	1.519	1.509	1.477	20b
gauche	3-21G	1.510	1.515	1.487	20b
		1.518			
s-cis	3-21G	1.519	1.507	1.488	20b
OH	DZ	1.498	1.525		22
OH_2^+					
perpendicular	DZ	1.498	1.524	1.451	22
bisected	DZ	1.501	1.512		22
O^-	DZ	1.525	1.532		22
CH_3	MW	1.514	1.514	1.513	52
	ED	1.509 (1)	1.509 (1)	1.517 (2)	53
	4-31G	1.517	1.519	1.500	27
ecl	4-31G	1.503	1.501	1.519	54
stagg	4-31G	1.502	1.504	1.506	54
ecl	4-21G	1.517	1.515	1.529	54
stagg	4-21G	1.515	1.518	1.516	54
1,1-$(CH_3)_2$	STO-3G	1.509	1.502	1.536	32
Li	4-31G(5-21G)	1.533	1.501	1.945	27
SiH_3	MW	1.520	1.508	1.853	49
	3-3-21	1.531	1.506	1.852	30
$C{\equiv}CH$	ED + MW	1.526 (7)	1.490 (14)	1.445 (8)	55

[a] Abbreviations: ED electron diffraction, MW microwave, DZ doubleζ basis set; the other basis sets are coded in the usual way, STO-3G, 4-21G, etc. [b] Taken from the survey in ref 8b. [c] Whiteside, L. A., Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon University: Pittsburg, PA, 1981. [d] Clark, T., private communication.

energetic consequences have not been explored adequately. The experimental data on simple cyclopropane derivatives is sparce,[9] and most of the calculational papers were concerned only with geometries and did not consider this important complementary aspect in any detail.[20-22,24,27-30] Dill, Greenberg, and Liebman's comprehensive theoretical examination of substituent effects on strain energies included 17 substituted cyclopropanes.[31] Unfortunately, only standard (nonoptimized) geometries and the minimal STO-3G basis set were employed. Especially for the "lone-pair" substituents this level of theory is inadequate, even when full optimization is carried out.[32] This problem has been emphasized recently by the same group.[23]

While these many studies have contributed significantly to our understanding, some confusion also has been promulgated. We show in the present paper that some of the "special" geometrical and energetic effects attributed to cyclopropane are not special at all but are found generally in unstrained alkanes as well. While

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(32) The STO-3G calculations being reported here date from before 1975. Problems with 1,1-difluorocyclopropane have been apparent for a decade; see: Bianchi, R.; Morosi, G.; Merguoli, A.; Simonetta, M. *Acta Crystallogr.* **1973**, *1329*, 1196 and the discussions in ref 23, 24a, and 24c.

Table II. MNDO, STO-3G, and 4-31G Geometries for Substituted Cyclopropanes

substituent	bond length, Å	MNDO	STO-3G	4-31G
H	CC	1.525[a]	1.502[b]	1.502[c]
Li	C_1C_2	1.533	1.523	1.533
	C_2C_3	1.528	1.497	1.500
	C_1Li	1.810	1.960	1.963
BeH	C_1C_2	1.537	1.522	1.531
	C_2C_3	1.517	1.494	1.490
	C_1Be	1.655	1.670	1.678
BH_2, bisected	C_1C_2	1.545	1.522	1.536
	C_2C_3	1.512	1.489	1.478
	C_1B	1.522	1.545	1.534
BH_2, perpendicular	C_1C_2	1.532	1.506	1.510
	C_2C_3	1.521	1.504	1.505
	C_1B	1.528	1.569	1.561
CH_3, staggered	C_1C_2	1.536	1.505	1.503
	C_2C_3	1.519	1.503	1.506
	$C_1C(H_3)$	1.513	1.528	1.510
NH_2, syn	C_1C_2	1.538		
	C_2C_3	1.522		
	C_1N	1.447		
NH_2, anti	C_1C_2	1.537	1.505	1.500
	C_2C_3	1.522	1.502	1.503
	C_1N	1.447	1.472	1.428
OH, syn	C_1C_2	1.541		
	C_2C_3	1.526		
	C_1O	1.377		
OH, anti	C_1C_2	1.540	1.507	1.492
	C_2C_3	1.525	1.511	1.517
	C_1O	1.381	1.419	1.408
F	C_1C_2	1.545	1.509	1.480
	C_2C_3	1.524	1.508	1.505
	C_1F	1.337	1.372	1.395

[a] See ref 35. [b] Footnote *c*, Table I. [c] Reference 49.

Table III. MNDO, STO-3G, and 4-31G Optimized Geometries of 2-Substituted Propanes[a]

substituent	parameter	MNDO	STO-3G	4-31G	exptl	
H	CC	1.530	1.541	1.530	(1.526)[b]	1.532[c]
	∠CCC	115.4	112.5	112.4	112.4	
Li	CC	1.527	1.551	1.543		
	CLi	1.840	2.037	2.032		
	∠CCC	116.5	108.9	109.7		
BeH	CC	1.537	1.552	1.548		
	CBe	1.680	1.709	1.711		
	∠CCC	114.1	109.9	110.1		
BH_2, bisected	CC	1.542	1.548	1.546		
	CB	1.560	1.580	1.577		
	∠CCC	113.4	111.0	110.0		
BH_2, perpendicular	CC	1.539	1.548	1.540		
	CB	1.557	1.580	1.574		
	∠CCC	112.6	111.0	111.2		
CH_3, staggered	CC	1.541	1.545	1.533		
	∠CCC	112.3	110.9	110.8		
NH_2, anti	CC	1.546	1.545	1.526		
	CN	1.475	1.492	1.460		
	∠CCC	112.6	111.4	111.4		
OH, anti	CC	1.551	1.551	1.523		
	CO	1.405	1.437	1.440		
	∠CCC	113.1	111.4	112.9		
OH, skew	C_1C_2			1.523		
	C_2C_3			1.515		
	CO			1.441		
	∠CCC			112.9		
F	CC	1.557	1.551	1.512		
	CF	1.359	1.388	1.430		
	∠CCC	113.1	111.7	114.5		

[a] Bond lengths in angstroms, bond angles in degrees. See supplementary material for full specification of those geometries. [b] Lide, D. R., Jr. *J. Chem. Phys.* **1960**, *33*, 1514. [c] Ijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1291.

its enhanced π-donor ability is unchallenged, cyclopropane functions exceptionally as a π-acceptor only in extreme cases. A full understanding of the interactions between cyclopropane and substituents also is important to help interpret the behavior of more complicated cyclopropane-containing systems (Figure 1). Furthermore, although many effects may be involved in bond-breaking reactions, it appears to be a good general rule that the longest ring bond is most easily cleaved, so that studies on the cyclopropanes themselves are useful in predicting reactivity.

We now report a "first-row sweep"[33] of monosubstituted cyclopropanes, C_3H_5X (X = Li, BeH, BH_2, CH_3, NH_2, OH, and F), fully optimized geometrically with the split-valence (4-31G) basis set. This is equivalent to the 4-21G and double-ζ basis sets which are shown by the data in Table I to reproduce experimental trends well over the whole set of substituents. For comparison we have also calculated all the corresponding 2-propyl compounds, 2-C_3H_7X. Such scans of the entire set of first-row substituents have helped to elucidate electronic effects for a number of ions and neutral species.[34] The same approach reveals significant trends for the cyclopropyl and 2-propyl compounds as well. The availability of structures and energies for a series of substituents of varying electronic properties calculated at a uniform and adequate level of theory should permit a definitive analysis of the effect of substituents on the geometries and energies of cyclopropanes. While we will concentrate on the 4-31G results, we also evaluate the performance of the STO-3G basis[32] and the MNDO method.[35] The latter semiempirical method allows the calculation of the larger systems typically investigated experimentally, and it is important to know if reliable results can be expected.

Quantum Mechanical Methods

MNDO[35] calculations were performed by using the standard program.[36] The ab initio calculations with the GAUSSIAN 76[37] series of programs used the STO-3G[38] minimal and 4-31G[39a] (and 4-31+G)[39b] split-valence basis sets. Geometry optimization was performed by using analytically evaluated atomic forces[40] in a Davidon–Fletcher–Powell multiparameter search routine.[41] The molecular orbital plots were produced by using Jorgensen's program[42] with STO-3G wave functions calculated with the 4-31G optimum geometries.

Results and Discussion

Geometries. The MNDO, STO-3G, and 4-31G optimum C_3H_5X optimum heavy atom bond lengths are compared in Table II. (Complete specifications of the 4-31G geometries and atomic coordinates are available as supplementary material.) Table III summarizes geometrical features of the corresponding isopropyl

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(42) Jorgensen, W. L. *QCPE* **1977**, *No. 340*. See also ref 14. A slight distortion of the ring to C_{2v} symmetry was used in Figure 2 MO plots in order to orient the degenerate orbitals consistently.

Table IV. ΔH_f (MNDO) and Total Energies (STO-3G, 4-31G)

X	ΔH_f, kcal/mol	total energies, au STO-3G// STO-3G	4-31G// 4-31G
cyclopropyl-X			
H	11.2[a]	−115.666 16	−116.883 86
Li	14.6	−122.365 99	−123.700 79
BeH	0.7	−130.095 28	−131.498 61
BH_2, perp.	16.3	−140.606 26	−142.090 53
BH_2, bis.	15.2	−140.615 51	−142.102 16
CH_3	4.0	−154.249 39	−155.864 31
NH_2, anti	14.6	−169.979 79	−171.826 15
NH_2, syn	16.2		
OH, exo	−32.5		−191.621 64
OH, endo	−32.7	−189.496 20	−191.621 34
OH, skew			−191.625 06
F	−34.2	−213.117 56	−215.611 11
2-propyl–X			
H	−24.9[a]	−116.886 42	−118.093 39
Li	−20.3	−123.572 66	−124.800 46
BeH	−29.6	−131.303 06	−132.697 31
BH_2, perp.	−14.3	−161.822 65	−143.297 94
BH_2, bis.	−13.9		−143.297 23
CH_3	−26.8	−155.466 84	−152.072 60
NH_2, anti	−16.3	−171.197 45	−173.034 15
NH_2, syn	−14.1		
OH, exo	−65.0		
OH, endo	−65.1	−190.716 84	−192.838 85
OH, skew			−192.839 38
F	−66.0	−214.337 96	−216.831 00

Table V. Stabilization Energies[a]

X	reaction 1	reaction 2	reaction 3
Li	8.3	2.1	−6.2
BeH	6.9	0.1	−6.8
BH_2, bisected	2.6	−6.5	−9.1
BH_2, perpendicular	2.1	+0.8	−1.3
CH_3	−2.3 (−4.9)[b]	−2.7 (−5.2)[b]	−0.8 (−0.3)[b]
NH_2, trans	−5.6 (−7.3)[b]	−6.5 (−6.6)[b]	−1.0 (0.8)[b]
OH, gauche	−8.6 (−9.8)[b]	−5.8	5.0
F	−11.8	−5.3	6.5

[a] 4-31G//4-31G in kcal/mol. [b] Experimental values in parentheses.

compounds. MNDO overestimates the C–C bond length in cyclopropane itself by 0.015 Å,[35] whereas STO-3G and 4-31G give bond lengths which are 0.008 Å too short (Table II).

All three methods predict lengthening of the C_1C_2 bonds and a shortening of the C_2C_3 bond when cyclopropane is substituted with one of the electropositive groups, Li, BeH, or BH_2. "Turning off" the π-acceptor effect in cyclopropylborane by rotating the BH_2 group by 90° from the more favorable bisected[43] to the perpendicular conformation gives an almost equilateral ring with C–C bond lengths close to those of cyclopropane itself. The C_1B bond length increases from 1.534 Å in the bisected conformation to 1.561 Å for the perpendicular rotamer (4-31G). Quite similar results have been obtained for the CH_2^+ substituent and to a lesser extent for NO_2 as well (Table I). The C_1–X bonds for X = Li, BeH, and BH_2 (bisected) are predicted by all three methods to be significantly shorter in cyclopropyl-X than in 2-propyl-X.

The CH_3 and NH_2 substituents have little effect on the ring C–C bonds, but the C–X distances are considerably shorter than in isobutane and 2-propylamine (Table III). The short (1.428 Å) C–N bond in cyclopropylamine (4-31G) agrees better with the earlier than the later interpretation of the microwave spectrum.[25] The Skancke–Boggs value (1.451 Å, Table I) is more satisfactory but was obtained by cyclic optimization.[27] We studied a number of amine conformations (see below) but were unable to locate a second, gauche minimum for cyclopropylamine although spectroscopic studies suggest that such a conformer exists.[26] The 4-31G and basis sets without polarization functions are known to underestimate inversion barriers of amines; further study at 6-31G* is indicated.

The greatest discrepancies between the three calculational methods (Table II) occur for cyclopropanol and cyclopropyl fluoride. MNDO predicts that the 1,2 bonds should be long and that the 2,3 bond length should be close to that in cyclopropane. STO-3G shows a slight lengthening of all bonds compared with C_3H_6. Only 4-31G reproduces the trend found experimentally for 1,1-difluorocyclopropane that the 1,2 bonds are shortened and the 2,3 bonds lengthened. The crude (but justifiable)[17] assumption that the cyclopropyl fluoride structure (which is not known experimentally) should be an average between 1,1-difluorocyclopropane and cyclopropane gives C_1–C_2 and C_2–C_3 bond lengths of 1.487 and 1.522 Å, respectively, in fair agreement with the 4-31G geometry. Similar results have been obtained with double-ζ basis sets (Table I). The gauche conformation found experimentally[44] for cyclopropanol is reproduced by 4-31G.

Energies. The MNDO heats of formation and ab initio total energies for the substituted cyclopropanes and 2-substituted propanes are shown in Table IV. These energies can be used for three important comparisons in the analysis of cyclopropane substituent effects; the methyl stabilization energies, defined by eq 1 and 2, identify the common stabilizing factors in 2-propyl and cyclopropyl derivatives, and eq 3 (a combination of eq 1 and 2) reveals the specific effects associated with the ring but not the acyclic systems.

$$CH_3X + CH_3CH_2CH_3 \rightarrow (CH_3)_2CHX + CH_4 \quad (1)$$

$$CH_3X + c\text{-}C_3H_6 \rightarrow c\text{-}C_3H_5X + CH_4 \quad (2)$$

$$(CH_3)_2CHX + c\text{-}C_3H_6 \rightarrow c\text{-}C_3H_5X + CH_3CH_2CH_3 \quad (3)$$

Table V summarizes the 4-31G//4-31G energies for these three reactions. The standard geometry STO-3G energies of Dill, Greenberg, and Liebman[31] as well as our own optimized STO-3G//STO-3G values for eq 3 show some substantial deviations. As expected from the difficulties with the geometries, these are especially large for the OH and F substituents. In evaluating eq 3, MNDO fails almost completely—all the substituents stabilize the cyclopropane ring to nearly the same extent!

The 4-31G data from Table V are presented as electronegativity plots in Figure 3. We find such plots to be useful for the interpretation of substituent effects.[45] The methyl stabilization energies of the 2-propyl derivatives (eq 1) are shown in Figure 3a. The plot shows the expected linear dependence of the stabilization energy on substituent heavy atom electronegativity[46] with no significant deviations attributable to differences in π-effects. A similar plot with a lower slope is found for CH_3X vs. C_2H_5X data.[45] Stabilization effects in 2-propyl derivatives, relative to methyl, can easily be understood by considering the extreme consequences of σ-electron donation or withdrawal. Complete donation from the substituent would give the carbanion; 2-$C_3H_7^-$ is less stable than CH_3^-. The highly ionic 2-C_3H_7Li and CH_3Li mirror this behavior closely. Complete electron withdrawal by the substituent would give 2-$C_3H_7^+$ and the much less stable CH_3^+. Hence, F and other electronegative substituents favor 2-propyl over methyl attachment. The methyl stabilization energy plot for cyclopropyl–X (Figure 3b) shows large deviations from the linear "σ only" line (roughly defined by the points for X = Li, perpendicular BH_2, H, and F). This line has a smaller slope than for 2-propyl–X, indicating that the electronegativity of the cyclopropyl group lies between those of methyl and 2-propyl. Again, the corresponding ions provide a basis for understanding. The cyclopropyl anion is calculated to be less stable than CH_3^- but more stable than 2-$C_3H_7^-$. The cyclopropyl cation is more stable

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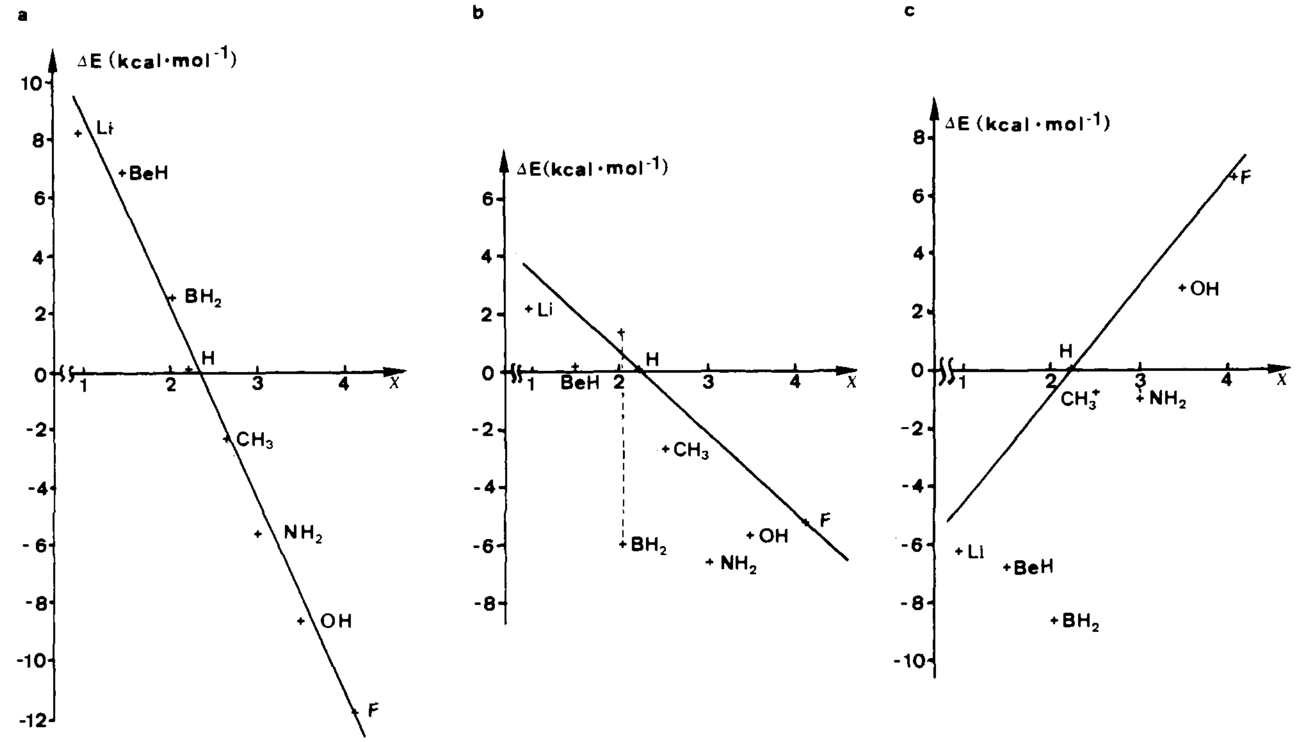


Figure 3. Plots of methyl stabilization energies vs. Pauling electronegativities of X in the XH_n groups. (a) 2-Propyl derivatives (eq 1). (b) Cyclopropyl derivatives (eq 2). (c) 2-Propyl vs. cyclopropyl substituent effects (eq 3).

than CH_3^+ but much less so than $2\text{-}C_3H_7^+$. Bisected BH_2 and NH_2 show large deviations from this line, indicating considerable π-stabilization. BeH, CH_3, and OH also show some extra stabilization. Figure 3c is redundant, but emphasizes the differences between 2-propyl and cyclopropyl and indicates which groups exhibit strong, non-σ effects. The plots suggest that the fluoride substituent, which has been used as the test for the effect of π-donors, behaves as a predominantly σ-substituent for the cyclopropane ring. Only the π-acceptors and strongest π-donors exhibit significant deviations in the order bisected BH_2 > BeH > trans NH_2 > skew OH.

Discussion

The interpretation of substituent effects on cyclopropane rings has focused mainly on geometry changes.[17] The energetic effects associated with cyclopropane substitution and a direct comparison with the energies and geometries of the corresponding 2-propyl derivatives allow a more comprehensive analysis of the problem. Figure 3 suggests strongly that the fluoride substituent behaves largely as a σ-acceptor with respect to the cyclopropane ring. Similar geometry changes in 2-fluoropropane as in cyclopropylfluoride are expected on this basis. This is verified by Figure 4, which shows a plot of the C_1C_2 bond lengths (4-31G) in cyclopropyl–X *vs.* the corresponding values in 2-propyl–X. Figure 4 is remarkably similar to Figure 3c. Clearly the factors affecting the energy and the geometry of cyclopropane derivatives are closely related. The substituents F, OH, CH_3, and perpendicular BH_2 (the non-π-acceptor conformation) define a straight line of slope 1.05 and clearly exert the same geometrical influence on the cyclopropyl group as on 2-propyl. In agreement with conclusions from Figure 3, only NH_2 and the π-acceptors should produce exceptional geometry changes which are specific to the cyclopropane ring. We shall now consider the orbital interactions responsible for both energy and geometry changes in cyclopropanes.

Figure 2 shows the four highest occupied and four lowest unoccupied MO's of cyclopropane ordered according to their energies. (A more nearly complete set is given by Jorgensen and Salem.[14]) The six Walsh MO's[13] are at the top. The additional degenerate 1e″ set, neglected in earlier qualitative discussions, is of obvious importance for σ-bonding. Since the 3e′ and 4e′ sets also are degenerate, we differentiate individual orbitals by "left" (L) and "right" (R) referring to the orientation in Figure 2; C_1 is at the left. We adopt and extend the designations of Durmaz and Kollmar,[22] π, π', and π'', as defined in Scheme I. π-Orbitals are antisymmetric with regard to C_s planes of monosubstituted cyclopropanes; π'-orbitals on the substituents are turned 90° from π-orbitals. The CCC ring is the nodal plane of π''-orbitals.

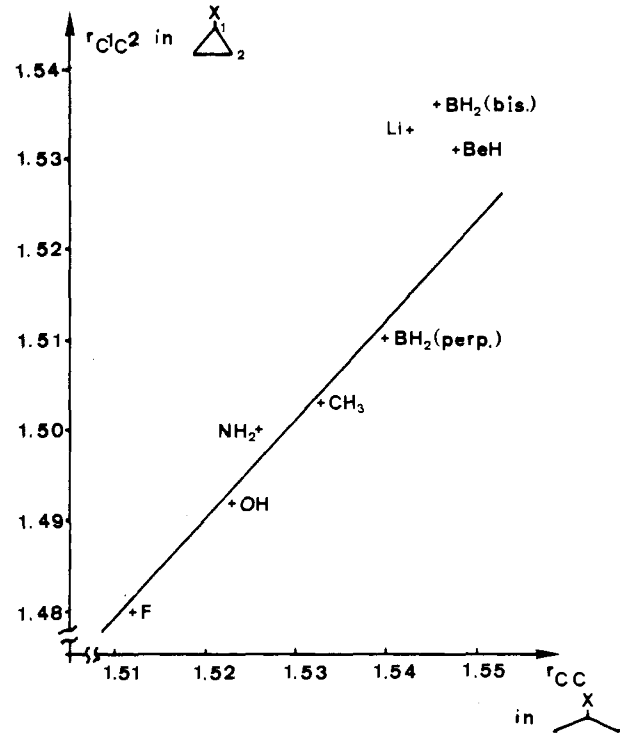
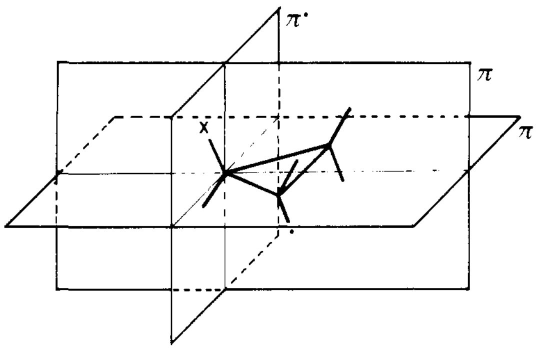


Figure 4. Plot of CC bond lengths in 2-propyl vs. the C^1C^2 distances in corresponding cyclopropyl derivatives.

The occupied orbitals of cyclopropane are influenced by substituents as follows. The 1e″ (R) MO has no contribution at C_1 and can be disregarded. Its 1e″ (L) counterpart, a π'' CH_2 MO

Scheme I



cyclopropane, has the largest coefficient at C_1 of any of the MO's shown in Figure 2 and is the most affected by the electronegativity of the substituent. This is the most effective σ-donor, a point not appreciated in earlier treatments. This 1e″ (L) MO is analogous to the $2b_1$ MO in propane,[14] and both should lead upon substitution to similar trends in energies, geometries, etc. This is exactly what we find (see below).

The degenerate Walsh 3e′ HOMO's are similar. By definition, 3e′ (L) has π′-symmetry, but the C_1 coefficients are small and, like the analogous $6a_1$ MO of propane,[14] can be disregarded. The predominate importance of the π-type 3e′ (R) MO was first pointed out by Hoffmann;[12] the analogous propane $4b_2$ MO is lower in energy and is much less effective than a π-donor.[47]

The acceptor orbitals of cyclopropane are analogous. The 4e′ (R) LUMO has π-symmetry but small coefficients at C_1. Its 4e′ (L) counterpart has the largest coefficients at C_1 and is low in energy. This is the most important π-acceptor orbital in cyclopropane, a point also not appreciated initially.[15,16] The $4a_2'$ MO was considered in this context, and incorrect predictions resulted. The $4a_2'$ MO is high in energy and appears to be effective only in exceptional cases, e.g., with the anionic substituents, O^- and CH_2^-,[22] but certainly not with F. Propane does not have any effective π- or π′-acceptor orbitals.

To summarize, the cyclopropane 1e″ (L) MO will be influenced most by σ-acceptors or σ-donors (electronegativity effects on coefficients). π-Acceptors will interact best with 3e′ (L) and π-donors with 4e′ (L) in a π′-manner. Antibonding interactions between donors and the occupied 1e″ orbital should result in little geometry change as no net electron transfer is involved. Definite predictions regarding the preferred conformations of substituents, energies, and CC ring bond lengths result. The 2-propyl effect should be mainly σ.

π-Acceptors. The effect of π-acceptors on cyclopropane geometries, first treated by Hoffmann,[15] is straightforward. Donation from the high-lying 3e′ (R) Walsh orbital, which is C_1C_2 bonding and C_2C_3 antibonding, leads to a lengthening of the C_1C_2 bonds and a shortening of the C_2C_3 bond. The most dramatic example is the cyclopropylcarbinyl cation (Table I),[11,12] which greatly prefers the bisected (π) over the perpendicular (π′) conformation. However, effects of appreciable magnitude also are exhibited by the BH_2 substituent. The cyclopropylborane rotation barrier is 7 kcal mol^{-1} at 4-31G; a value of 4.2 kcal mol^{-1} has been found experimentally for cyclopropyldifluoroborane.[48] NMR data also indicate a preference for the bisected conformation.[49] The deviations of the bisected BH_2 values, but not those for the perpendicular conformations in Figures 1b, 1c, and 2, show the operation of the π_{BH_2}-effect clearly. Possible π′-interactions do not appear to be significant as shown by the small BH_2 rotational barrier and geometry differences in the 2-propylborane conformations.

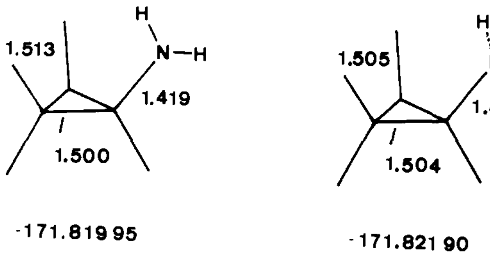


Figure 5. Geometries and 4-31G//4-31G energies of perpendicular and bisected aminocyclopropane isomers with planar NH_2 groups.

σ-Acceptors. σ-Acceptors withdraw electron density from the 1e″ (L) cyclopropane MO. This orbital is C_1C_2 antibonding and C_2C_3 bonding. The effect of σ-acceptors should therefore be exactly the opposite to that of π-acceptors (i.e., to shorten the C_1C_2 bonds and to lengthen the C_2C_3 bond). This effect is, however, equivalent to the corresponding interaction in 2-propyl derivatives so that similar geometry changes can be expected (Figure 4). The energetic effects are larger for cyclopropane, however. Fluorine substituents do not act as π-donors, as originally assumed,[15,16] but predominantly as σ-acceptors. The geometries,[7] reactivity,[5] and destabilization[23] of fluorocyclopropanes can be explained on this basis. The effect of σ-acceptors can be considered to be indirect as the 1e″ (L) orbital is involved more with C–H bonding than with CC interactions as the 1e″ (L) orbital is π_{CH_2} in character and involved more with C–H bonding than with CC interactions. Nevertheless, removal of electrons will have the geometrical effects described. The large effects of difluoro substitution (Table I) are due to such π″-interactions.

σ- and π-Donors. The 4e′ LUMO of cyclopropane with a significant contribution at C_1 can act as a σ- or a π′-acceptor. This orbital is C_1C_2 antibonding and C_2C_3 bonding, so that donation results in a lengthening of the C_1C_2 bonds and a shortening of the C_2C_3 bond, exactly the same effects as found for π-acceptors. The amino group in cyclopropylamine prefers a s-trans, pyramidal conformation, which confirms that the most effective cyclopropane acceptor orbital is of the π′ type, i.e., 4e′ (L). The geometries obtained for cyclopropylamine model calculations with the amino group held planar are shown in Figure 5. The bisected isomer is the least stable, 1.2 and 3.9 kcal mol^{-1} higher in energy than the perpendicular and best (trans, pyramidal) conformations. These results agree with prior calculations and experiments. The ring distortion of the bisected conformation is not very pronounced and is characteristic of a weak σ-acceptor. The perpendicular conformation, in which the amino group can interact with the π′-acceptor, has an almost equilateral ring with CC distances almost unchanged from those of cyclopropane or of the best geometry of cyclopropylamine (Tables I, II).

The best σ-donor, Li, lengthens the vicinal cyclopropane bond and leaves the distal bond unchanged. In the cyclopropyl anion, optimized at the diffuse function augmented level (4-31+G),[39b] both C–C bonds are lengthened, the distal less so. As mixing of the 1e″ (L) and 4e′ (L) MO's is involved here, the situation is somewhat more complex but can be visualized by examining the HOMO of the isoelectronic aziridine (8a′).[14] This mixing results in greater vicinal bond lengthening. In 2-propyllithium there is a corresponding widening of the CCC angle, and the C–C bonds also are longer.

Conclusions

The σ-acceptor order, methyl > cyclopropyl > 2-propyl, and the order of σ-donating ability, 2-propyl > cyclopropyl > methyl, govern the underlying trends in stabilization energies (Figure 3) and geometries (Figure 4) produced by substituents. These trends are similar for cyclopropyl and 2-propyl systems but are of different magnitudes when compared to methyl. Cyclopropane

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Table VI

substituent type	main cyclopropane MO involved	C_1C_2 vicinal	C_2C_3 distal	favored substituent conformation
π-acceptor	3e′(R) π-type	longer	shorter	bisected
π-donor	4e′(L) π′-type	longer	shorter	perpendicular
σ-acceptor	1e″(L)	shorter	longer	
σ-donor	1e″(L)	longer	shorter	

π-interactions can be regarded as perturbing effects and have been overemphasized in the past, especially for fluorine substituents which function as σ-acceptors and not as π-donors.

As has long been appreciated,[4,5,11-17] cyclopropyl is a fairly strong π-donor and is stabilized by π-acceptor substituents but only in bisected conformations. Cyclopropyl is less effective as a π-acceptor, but strong π-donor substituents lead to some stabilization by interaction with the 4e′ (L) LUMO, the main acceptor orbital. This orbital is a π′-acceptor, as defined above, and favors orientations of substituent lone-pair orbitals in the C_s C_3H_5X plane. Thus, cyclopropylamine prefers trans and cyclopropanol skew conformations. Contrary to earlier interpretations, the $1a'_2$ Walsh orbital is not of major importance (with the possible exception of negatively charged substituents, e.g., O^-, and bisected CH_2^-).[22]

Although any given substituent will interact significantly with several cyclopropane orbitals, it is useful to identify the principle effects. These can be used in a simple way to predict changes in bond lengths and favored conformations, as summarized in Table VI.

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Registry No. $(CH_3)_2CH_2$, 74-98-6; *i*-PrLi, 1888-75-1; *i*-PrBeH, 90823-09-9; *i*-$PrBH_2$, 17643-29-7; $(CH_3)_3CH$, 75-28-5; *i*-$PrNH_2$, 75-31-0; *i*-PrOH, 67-63-0; *i*-PrF, 420-26-8; cyclopropyllithium, 3002-94-6; cyclopropylhydroberyllium, 84064-91-5; cyclopropylborane, 72507-58-5; methylcyclopropane, 594-11-6; cyclopropanamine, 765-30-0; cyclopropanol, 16545-68-9; fluorocyclopropane, 1959-79-1.

Supplementary Material Available: Complete 4-31G optimized geometries and coordinates for the cyclopropyl and 2-propyl derivatives (18 pages). Ordering information is given on any current masthead page.

Transient EPR and Magnetophotoselection in the Photolytic Formation of a Trimethylenemethane Biradical

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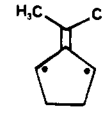
Abstract: The transient EPR response of the triplet biradical 2-isopropylidenecyclopenta-1,3-diyl accompanying its production by pulsed laser photolysis at 337 nm reveals that the biradical is born predominantly in the T_z zero-field substate and the coupling constant *D* is positive. Magnetophotoselection experiments demonstrate that the electric dipole transition moment in the diazene precursor is parallel to the in-plane magnetic axis which yields the smallest of the three high-field spin–spin splittings. Symmetry considerations bearing on the results are presented.

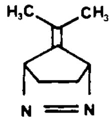
Processes which carry a molecule between its singlet and triplet manifolds are usually state selective: i.e., crossing from a given singlet state to only one of the three triplet sublevels usually predominates. Many instances of the phenomenon have been uncovered in studies of the population and depopulation of photoexcited triplets. In solid solutions of some aromatic molecules in crystalline hosts such as fluorene or benzoic acid, state selectivity is preserved to temperatures just below the melting point of the hosts. CIDEP phenomena in liquids demonstrate the persistence of the selectivity in fluid media.

In contrast to the many studies of triplet–singlet interconversions in which a single molecular species evolves with no change in molecular composition among states accessible to it, there have been to our knowledge only a few reported instances of state selectivity in chemical processes in which a singlet precursor is irreversibly disrupted to yield a triplet product.[1,2]

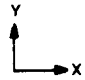
In each of the cited cases the triplet product is born predominantly in only one of its zero-field eigenstates. The eigenstates in an external magnetic field are superpositions of the zero-field ones. Their populations at instant of birth are determined by their composition. We report here our studies of the formation of the biradical **1** by photolysis of the diazene **2**.



1



2



Experimental Section

Transient Experiments. The diazene **2** in rigid isotropic solution in methyltetrahydrofuran or octafluorotoluene was photolyzed at 77 K in the cavity of an X-band EPR spectrometer by light from a nitrogen laser, λ 337 nm, pulse duration 10 ns, pulse energy less than 1 mJ.

The transient responses at the fields at which the conventional CW spectra (derivative of absorption with respect to magnetic field vs.

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