

β -Substituted Cyclopropyl Radicals

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Ab initio and MNDO molecular orbital calculations support experimental evidence that 2-metallo-substituted cyclopropyl radicals prefer *cis*- while 2-halogenocyclopropyl radicals prefer *trans*-configurations.

The formation of predominantly *trans*-1,2-dibromocyclopropane in Hunsdiecker reactions of cyclopropane-1,2-dicarboxylates suggests a preference of the intermediate 2-bromocyclopropyl radical for the *trans*-conformation.¹ The results of Grignard reactions on 1,2-dibromocyclopropanes, on the other hand, indicate that *cis*-2-magnesium-substituted cyclopropyl radicals might be more stable than the *trans*-forms.² We have now calculated geometries and energies of these conformationally locked β -substituted alkyl radicals³⁻⁵ with *ab initio* molecular orbital theory.[†]

Optimisations with the 3-21G basis set⁶ (33-21G for Mg and Cl)⁷ were carried out for *cis*- and *trans*-2-substituted cyclopropyl radicals with the substituents F, Cl, Li, and MgH. The energies are summarised in Table 1, and the geometries in Scheme 1. The *trans*-2-fluorocyclopropyl (1) and *trans*-2-chlorocyclo-

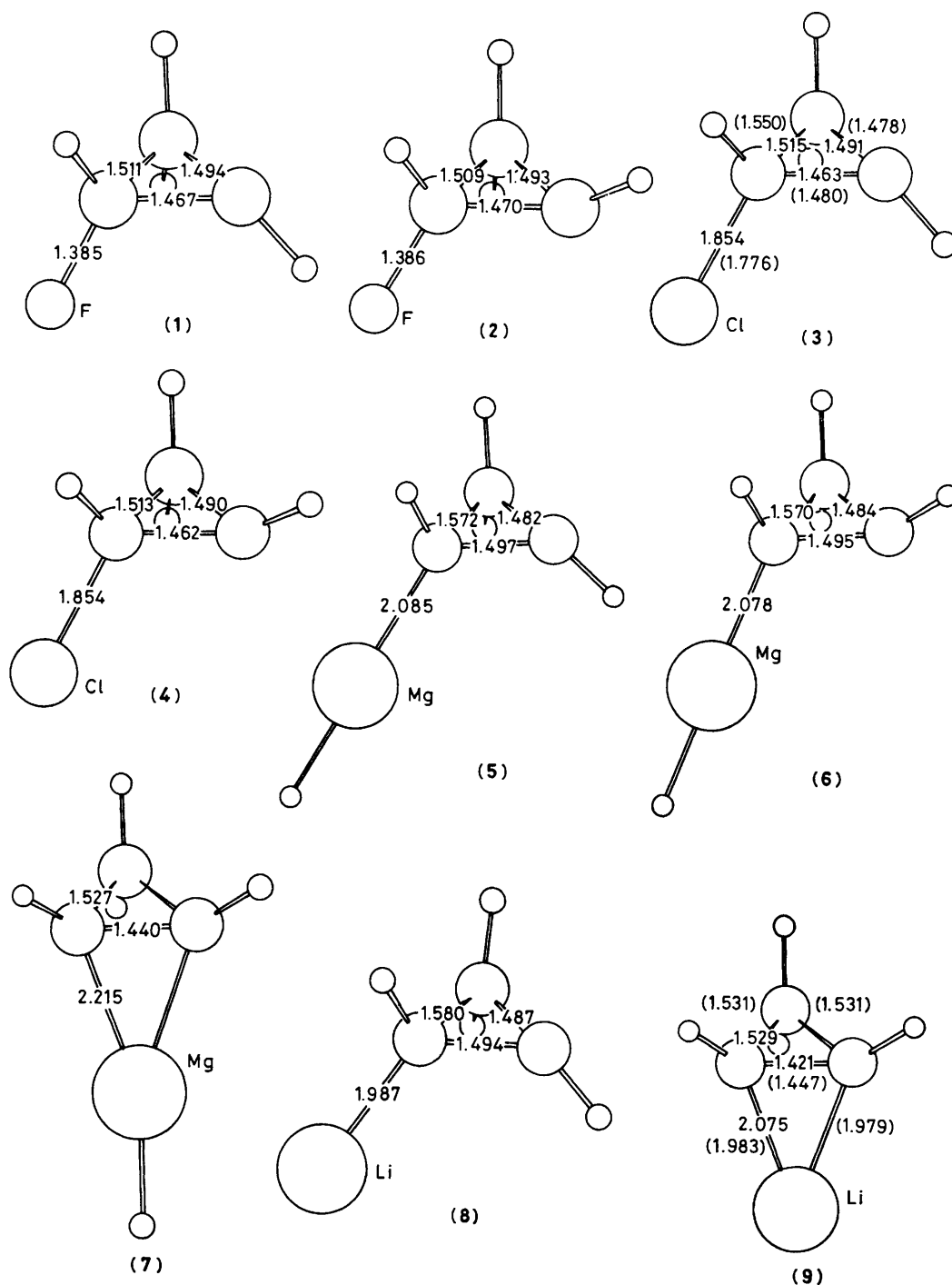
Table 1. Total (a.u.) and relative (kcal/mol) 3-21G energies.^a

	Total energy	Relative energy
2-Fluorocyclopropyl	(1) -214.06989	0.0
	(2) -214.06821	1.1
2-Chlorocyclopropyl	(3) -572.47137	0.0
	(4) -572.47011	0.8
2-(MgH)-cyclopropyl	(5) -314.19609	1.6
	(6) -314.19857	0.0
	(7) -314.18755	6.9
2-Lithiocyclopropyl	(8) -122.53778	3.6
	(9) -122.54354	0.0
Fluorocyclopropane	-214.71613	—
Chlorocyclopropane	-573.11608	—
Cyclopropylmagnesium hydride	-314.83653	—
Cyclopropyl-lithium	-123.17584	—

[†] All calculations used the Gaussian 76 series of programs (J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, 'Quantum Chemistry Program Exchange,' Program No. 368, Indiana University, 1978). Radicals were calculated using the unrestricted Hartree-Fock (UHF) formalism and closed shell molecules with restricted Hartree-Fock (RHF). Optimisations used analytically evaluated atomic forces (H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, 1975, **63**, 3622) in a Davidson-Fletcher-Powell multiparameter search routine (W. C. Davidon, *Comput. J.*, 1968, **10**, 406; R. Fletcher and M. J. Powell, *ibid.*, 1963, **6**, 163; D. Poppinger, *Chem. Phys. Lett.*, 1975, **34**, 332). The molecular orbital plots (ref. 11) used RHF/STO-3G wavefunctions. Singly occupied MO's are plotted as if they were doubly occupied. MNDO calculations (M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899) used a preliminary parameter set for lithium (W. Thiel and T. Clark, unpublished results).

^a The total energies for the other species in equations (1) and (2) are taken from the CMU Quantum Chemistry Archive (ref. 13).

propyl (3) radicals are calculated to be marginally more stable (by 1.1 and 0.8 kcal/mol, respectively) (1 kcal = 4.18 kJ) than the *cis*-forms, (2) and (4). This behaviour mirrors the *transoid* structure found in e.s.r.⁸ and theoretical⁹ studies on the β -chloroethyl radical. The magnesium-substituted radicals, (5) and (6), show no unusual geometrical features. The *cis*-isomer (6) is calculated to be 1.6 kcal/mol more stable than *trans*-(5). The bridged C_s structure (7) was also calculated (in analogy to 2-lithiocyclopropyl), but was found to be 6.9 kcal/mol less



Scheme 1

Table 2. 3-21G reaction energies (kcal/mol).

X		ΔE^a	ΔE^b
F	(1)	+1.0	+39.5
Cl	(3)	+0.1	+20.6
Li	(9)	-7.7	+0.1
MgH	(6)	-4.2	+20.4

^a Equation (1). ^b Equation (2).

stable than (5). *trans*-2-Lithiocyclopropyl (8) is also found to prefer a classical structure, but optimization of the *cis*-isomer gives the bridged structure (9), (C_s), which is 3.6 kcal/mol lower in energy than (8).

Isodesmic reactions involving the 2-substituted cyclopropyl radicals give the stabilisation energies due to the substituent, equation (1). The dissociation energies, equation (2), are another indication of the stability of the radical.

The 3-21G energies for these reactions (Table 2) show the

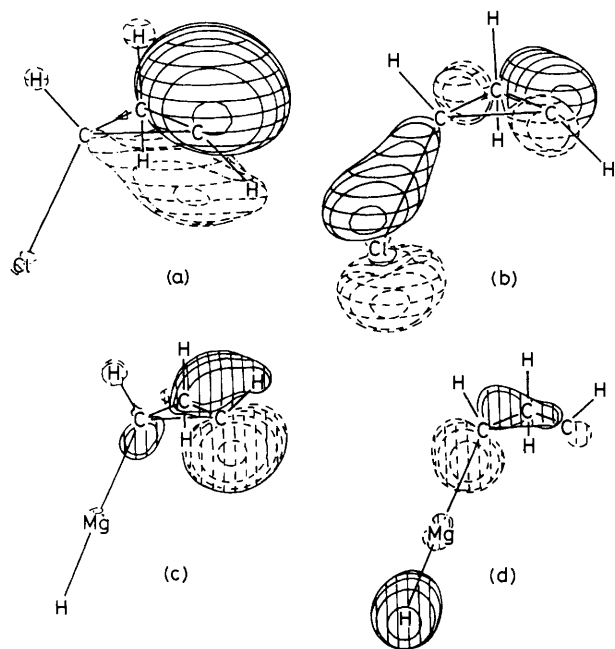
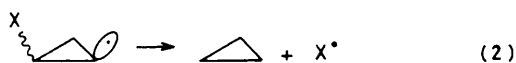
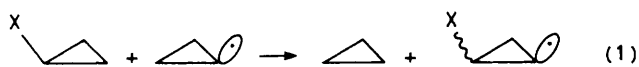


Figure 1. (a) The singly occupied molecular orbital (SOMO) of (3) (contour level $0.06 \text{ e}^-/\text{\AA}^3$). Note the interaction with the β -CH, rather than the CCl, bond. (b) The σ_{CCl} orbital of (3) (contour level $0.1 \text{ e}^-/\text{\AA}^3$). This orbital shows the involvement of a ring Walsh orbital, but not of the SOMO. (c) The SOMO of (6) (contour level $0.06 \text{ e}^-/\text{\AA}^3$). There is significant delocalisation to the β -carbon. (d) The σ_{CMg} orbital of (6) (contour level $0.1 \text{ e}^-/\text{\AA}^3$). The bonding interaction with the SOMO can be seen from the delocalisation to the α -carbon.

fluoro- and the chloro-radicals to be slightly destabilised relative to cyclopropyl, but bound with respect to dissociation into cyclopropene and a halogen atom. The lithium radical (9), while stabilised relative to cyclopropyl, is only just bound relative to cyclopropene and a lithium atom. The magnesium substituted radical (6) is both stabilised relative to cyclopropyl and strongly bound with respect to dissociation into cyclopropene and MgH^{\bullet} . Hence, the formation of 1,2-dilithiocyclopropane from 1,2-dibromocyclopropane and lithium may be much less successful than the corresponding Grignard reaction.¹⁰

The molecular orbital plots¹¹ (Figure 1) show the origin of these geometrical preferences. Donation from the backside of the σ_{CMg} orbital in (6) to the radical SOMO gives a three-electron interaction which is stabilising because of the partial negative charge on C(2).¹² Such stabilisation is not possible for the chlorine substituted radicals as C(2) is partially positively charged. While a one-electron interaction between the SOMO and the σ_{CCl}^* could lead to an energy lowering, this evidently is not significant. It would lead to a preferred

cis-conformation and to a net stabilisation, neither of which is observed. The MO plots (Figure 1) suggest that the interaction between the β -CH bond and the radical is more important than any overlap involving a halogen. The inductive effect of chlorine leads to a slight destabilisation of the radical. Figure 1 shows clearly that the σ_{CCl} orbital interacts with a ring Walsh orbital, rather than with the SOMO. Thus, although the UHF total spin density and e.s.r. studies on 2-chloroethyl⁸ show some spin on chlorine this is more a spin polarisation effect than evidence for extensive delocalisation.

MNDO calculations were performed for (3), (4), and 2-lithiocyclopropyl; the results are in agreement with the *ab initio* calculations and demonstrate that MNDO gives qualitatively reliable results in such systems. Both (3) and (4) converged to the optimized structure (3) ($\Delta H_f = 46.2 \text{ kcal/mol}$); the *cis*- and *trans*-isomers of 2-lithiocyclopropyl converged to the bridged structure (9) ($\Delta H_f = 51.2 \text{ kcal/mol}$). The parameters of (3) and (9) are shown in parentheses in Scheme 1.

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