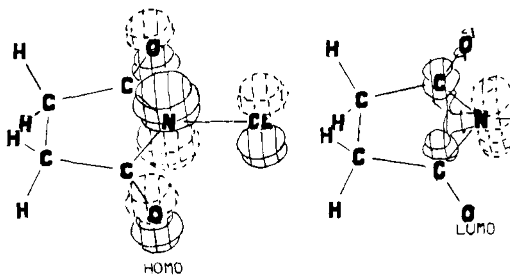


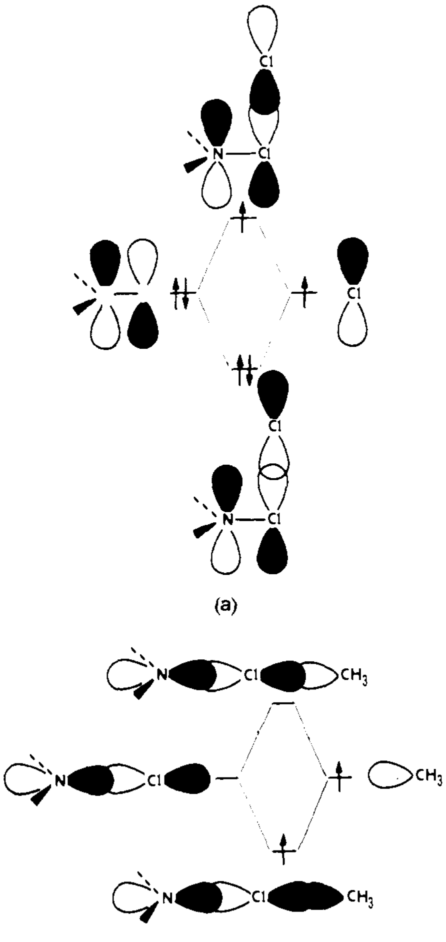
Figure 1. The frontier orbitals of *N*-chlorosuccinimide.

preferred direction of attack is colinear with the NCl bond and further reaction leads to formation of the σ_N succinimidoyl radical via involvement of the lower lying σ_{NCl} orbital.

MNDO reaction path calculations confirm these predictions. A chlorine atom gives initial attack from above the NCS molecule, practically on a line from chlorine perpendicular to the mean molecular plane. This reaction yields the π radical and is calculated to be exothermic by 14.6 kcal mol^{-1}, with an activation energy of 7.2 kcal mol^{-1}. The methyl radical, however, gives initial attack colinear with the NCl bond, yielding σ_N succinimidoyl in a reaction which has an activation energy of 14.6 kcal mol^{-1} and which is exothermic by 0.8 kcal mol^{-1}.

Reaction paths calculated using initial attack by $CH_3\cdot$ perpendicular to the NCS plane collapsed to the colinear attack path. When Cl approaches from exactly the line of the NCl bond, an electronic state which correlates with the σ_O succinimidoyl radical is obtained. This approach leads to a steep increase in energy but no reaction. If the Cl· atom is initially placed slightly away from the N–Cl axis, the reaction path collapses to one identical with that calculated for initial attack perpendicular to the plane.

Scheme I



(a)

(b)

The orbital situation outlined above is by no means uncommon, so that Skell's suggestion[1] that there may be more cases of excited-state radical generation is almost certainly correct. The search for further examples can, however, be greatly facilitated by preliminary screening of likely precursors by molecular orbital theory.

Acknowledgments. The author thanks Professor P. v. R. Schleyer for support and encouragement and Dr. J. Chandrasekhar and Dr. P. Hofmann for helpful discussions. This work was facilitated by the cooperation of the staff of the Regionales Rechenzentrum Erlangen.

Supplementary Material Available: Summaries of MNDO results for NCS and the two succinimidoyl radicals (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) See Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978,** *11,* 381, and references therein.

(2) INDO calculations (Koenig, T.; Wielesek, A. *Tetrahedron Lett.* **1975,** 2007) suggest that the σ_O radical may also be low in energy. We have been unable to calculate this species directly,[11] but the reaction paths give only the π and σ_N radicals.

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(9) The molecular orbital plots actually used RHF/STO-3G wave functions. Jorgensen's plotting program (see Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973) was extended to include second-row elements by Dr. M. B. Krogh-Jespersen and Dr. J. Chandrasekhar.

(10) At RHF/STO-3G the NCS LUMO is a π^*_{CO} combination with very little contribution at N and Cl. This orbital is, however, close in energy to the σ^*_{NCl}, as it is at MNDO. The HOMO and LUMO discussed here refer to the orbitals shown in Figure 1. The order of the π^*_{CO} and σ^*_{NCl} orbitals has *no* effect on the arguments presented in the mechanistic discussion.

(11) The half-electron method is not well suited for the calculation of excited-state radicals, and this is not usually possible with our present version of the MNDO program. In this case, however, the σ_N radical can be obtained by use of a suitable starting geometry.

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Received June 27, 1979

The Carbenoid, CCl_3Li, Eschews Tetrahedral Structures

Sir:

Both reactivity[1,2] and matrix isolation studies[3,4] suggest the carbenoid, CCl_3Li, to exist in more than one isomeric form. Our calculations on the prototype carbenoid, CH_2FLi, revealed three separate minima (isomers),[5] none of which conforms to conventional structural rules for organic molecules. We have now continued our quest for unusual geometries of carbon compounds[6] by investigating CCl_3Li by ab initio molecular orbital theory.[7] Our results indicate the *triply bridged* species (**1**), with lithium situated on the "wrong side" of the molecule, to be the most stable form of CCl_3Li!

Geometry optimization of a $Cl_2C{:}ClLi$ complex of C_s symmetry, analogous to one of the minima of H_2CFLi,[5] led to **1** (C_{3v}). The most stable form of CH_2FLi[5] has its counterpart in **2**. **3**, a $Cl_2C{:}LiCl$ complex, is the third local minimum on the potential energy surface at both the minimal basis STO-3G[8] and split-valence basis 4-31G[9] levels. The geometry of the

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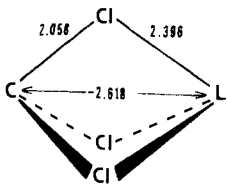
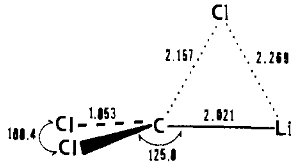


1



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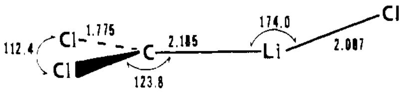

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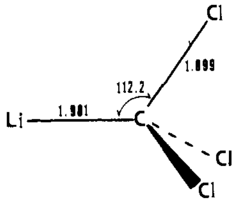

4

"classical" structure, **4,** could only be optimized by imposing C_{3v} symmetry. **4** is *not* a local minimum; when the symmetry constraint is removed, **2** results. The 4-31G optimized geometries are shown in **1–4.**

The STO-3G and 4-31G total and relative energies are given in Table I. Included are single point STO-3G* calculations carried out on the STO-3G geometries. The STO-3G* basis set includes a set of d orbitals on chlorine; since the relative energies of **1–4** changed very little from those at STO-3G, we did not optimize the structures at STO-3G*. Although the energy differences are smaller at 4-31G (Table I), the ordering of **1–4** remains the same with all basis sets used. **1** is significantly more stable than any of the other forms.

1 is remarkable. Andrews[3] observed a species with C_3 symmetry (presumably C_{3v}) to be the most stable form of CCl_3Li. Who would have considered **1,** rather than **4,** to be the correct structure of this species? With hindsight, **1** does not appear unreasonable. The observed C–Cl force constants in CCl_3Li were rather low and were attributed to a high degree of ionic character.[3] CCl_3^- should be a pyramidal species (Cl–C–Cl = 101.9° at 4-31G) with the negative charge delocalized to the electronegative chlorines. These halogens are already richly endowed with lone pairs. Little wonder that Li^+ prefers the chlorine side of the CCl_3 pyramid, where triple bridging can occur.

CCl overlap populations are calculated to decrease in the order $CCl_4 > \mathbf{4} \gg CCl_3^- > \mathbf{1}$, so that either **1** or CCl_3^- would show the observed low force constants.[3] However, as stretching frequencies involving lithium are also observed,[3] CCl_3^- can be ruled out. The only alternative to **1** with C_{3v} symmetry is **4,** which, even if it were a local minimum, has C–Cl bonds almost as strong as those in CCl_4.

Andrews[4] suggested **3** to be the second CCl_3Li isomer. Both **2** and **3** are close in energy at 4-31G (Table I) and both might yield infrared spectral features in accord with those observed for this second species.[4] Although we cannot rule out **3**, **2** is calculated to be more stable than **3** at all levels of theory used so far.

Structures **1** and **2** can also be taken to represent the two modes of ionic dissociation suggested by Köbrich for carbenoids.[10] **2** is analogous to the $CH_2Li^+F^-$ ion pair found previously[5] and need not be discussed further. **1**, on the other hand, can be considered to be a $CCl_3^-Li^+$ ion pair. The significant Cl–Li overlap population in **1** (0.16 STO-3G) and the slightly decreased CCl overlap population relative to CCl_3^- (0.27 vs. 0.30) suggests, however, that multicenter covalent bonding also helps determine the structure of **1**. The C–Cl bonds in **1** are longer than in CCl_3^- (2.058 vs. 2.015 Å at 4-31G) and the Cl–C–Cl angles are smaller (97.5° in **1** vs. 101.9° in CCl_3^- at 4-31G). The C–Li distance (2.62 Å, 4-31G) is long relative to that in CH_3Li (1.99 Å); C and Li are antibonding with respect to each other (overlap = −0.04). The bonding consists of three very polar C–Cl–Li bridging bonds in which the C–Cl overlap is much more significant than Cl–Li.

Table I. Total[a] and Relative[b] Energies for the CCl_3Li Isomers **1–4**

structure	STO-3G// STO-3G	STO-3G*// STO-3G	4-31G//4-31G
1	−1408.488 56 (0.0)	−1408.550 44 (0.0)	−1422.209 99 (0.0)
2	−1408.474 05 (+9.1)	−1408.537 82 (+7.9)	−1422.207 63 (+1.5)
3	−1408.468 20 (+12.8)	−1408.531 40 (+12.0)	−1422.203 38 (+4.1)
4	−1408.450 32 (+24.0)	−1408.510 42 (+25.1)	−1422.199 63 (+6.5)

[a] In hartrees (≡627.49 kcal/mol). [b] In parentheses (kilocalories/mole).

Note Added in Proof. We have now found yet another minimum on the CCl_3Li potential surface: a C_s structure, **5,** with two bridging chlorines and a short C–Li bond; the third chlorine forms an almost linear Cl–C–Li unit. **5** is comparable in stability with **3** at all three basis set levels and so does not affect the conclusions regarding the species observed in the matrix.

Seebach et al.[11] have reported the ^{13}C NMR spectra of *two* CBr_3Li species in solution. Both species show very large ^7Li–^{13}C coupling constants; this rules out a type **1** structure. Extrapolation from our calculated (4-31G) results on CF_3Li[12] and CCl_3Li suggests that a species corresponding to **2** might be the most stable form of CBr_3Li, and that this may be one of the observed species. The second species observed may correspond to a structure of type **4**, which is calculated to be a minimum when solvated with one molecule of ammonia,[12] or a structure of type **5.**

Acknowledgments. This work was supported by the Fonds der Chemischen Industrie and was assisted by a NATO Grant. We thank D. Poppinger, H. B. Schlegel, and J. Chandrasekhar for program developments which facilitated the calculations and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

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Received September 12, 1979