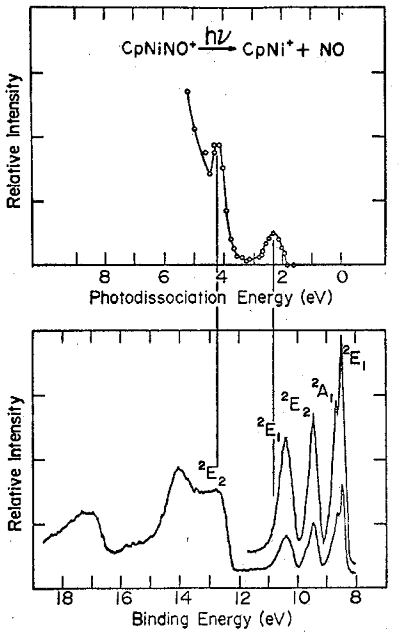

**Figure 1.** Comparison of the photodissociation spectrum of CpNiNO$^+$ to the photoelectron spectrum of CpNiNO. The energy axis of the photoelectron spectrum is adjusted such that the first adiabatic ionization potential of CpNiNO is zero on the photodissociation energy scale.

photodissociation for determining upper limits on metal–ligand bond energies.[13] The technique will not only aid complementary methods such as photoionization but also in some instances may be the only way to make the measurement, especially in those systems where a stable, neutral parent molecule is difficult to generate. We are currently investigating the photochemistry of CpNi$^+$ bound to a range of n- and $\pi$-donor bases to determine upper limits on bond dissociation energies and the effect of various bases on the transitions observed. In addition, experiments on methyl-substituted CpNiNO, where substitution lowers the ionization potential of electrons localized on the cyclopentadienyl moiety relative to those on the metal, will clarify the tentative transition assignments and photoelectron orbital assignments reported above.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, to the Research Corp. under a Cottrell Research Grant, and to Du Pont for support administered through Purdue University.

**Registry No.** CpNiNO$^+$, 60507-93-9.

## References and Notes

(1) T. A. Lehman and M. M. Bursey, "Ion Cyclotron Resonance Spectrometry", Wiley-Interscience, New York, 1976.
(2) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(3) D. A. McCrery and B. S. Freiser, *J. Am. Chem. Soc.*, **100**, 2902 (1978).
(4) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 3214 (1977).
(5) T. E. Orlowski, B. S. Freiser, and J. L. Beauchamp, *Chem. Phys.*, **16**, 439 (1976).
(6) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 3136 (1976).
(7) R. C. Dunbar and B. B. Hutchinson, *J. Am. Chem. Soc.*, **96**, 3816 (1974).
(8) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 3671 (1974).
(9) S. Evans, M. F. Guest, I. H. Hillier, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, **70**, 417 (1974).
(10) R. R. Corderman and J. L. Beauchamp, submitted for publication in *J. Am. Chem. Soc.*
(11) R. R. Corderman and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 3998 (1976).
(12) A 3.5-kW mercury–xenon arc lamp was used in conjunction with a Schoeffel 0.25-m monochromator. Two gratings were employed in order to cover the full wavelength range. A cutoff filter was also used at long wavelengths to eliminate second-order radiation from the monochromator.
(13) Photodissociation yields only an upper limit on the metal–ligand bond energy since an absorption band may not lie at an energy in the vicinity of the thermodynamic threshold for dissociation. For CpNiNO$^+$, an absorption band does occur in the thermodynamic threshold region.

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

**Robert C. Burnier**
**Ben S. Freiser***

*Received June 28, 1978*

---

## Molecular Structure of Tetracyclohexylsilane

*Sir:*

In species of the type R$_4$M, where R is a twofold rotor, the molecular symmetry must be a subgroup of $D_{2d}$[1] and is usually found to be $S_4$. This is the case for the tetraphenyl compounds of C,[2] Si,[3] Ge,[4] Sn,[5] and Pb,[6] for tetraphenylphosphonium,[7] -bismuthonium,[8] and -arsonium[9] ions, for tetrakis(pentafluorophenyl) compounds of Si,[10a] Ge,[10b] and Sn,[10b] for tetrakis(4-methylphenyl)tin,[11] tetranitromethane,[12] tetraphenylborate,[13] and, to a close approximation, for tetramesitylvanadium.[14] This marked preference for $S_4$ symmetry is maintained even when the local symmetry of the ligand R is lowered from (essentially) $C_{2v}$ to $C_s$; in that case, the most stable arrangement seems to be one in which the four R groups arrange themselves in an all-exo conformation,[1] leading to molecular $S_4$ symmetry. This is what is found by X-ray crystallography for tetrakis(3-methylphenyl)tin[15] and for the tetra-2-thienyl compounds of Si,[16a] Ge,[16b] Sn,[16b] and Pb[16b] and what is found by empirical force field calculations[1] for tetrakis(2-methylphenyl)methane and -silane.

In light of this overwhelming predilection for $S_4$ symmetry, a recent report[17] that tetracyclohexylsilane (**1**) assumes a $C_2$ conformation takes on special significance. The purpose of this communication is to demonstrate that although the exact crystallographic symmetry of **1** is $C_2$, the molecular conformation is in fact very near $S_4$ and therefore fits into the general pattern described above.

Starting from a $D_{2d}$ conformation (Figure 1, top),[18] we can obtain a structure with $D_2$ symmetry by twisting all four cyclohexyl groups in the same sense and to the same extent. A structure with $S_4$ symmetry is obtained by twisting pairs of groups to the same extent but in opposite directions. To obtain $C_2$ symmetry, the pairs of groups must be twisted to different extents. In the reported[17] X-ray structure of **1**, two of the dihedral angles, C(2)–C(1)–Si–C(1$^a$) and C(8)–C(7)–Si–C(7$^a$) (cf. Figure 1, bottom), were found to have values of −56.2 and −71.0°, respectively, from which it was concluded[17] that two of the rings were "twisted by about 15° from an "idealized" $S_4$ conformation". However, these two dihedral angles are not related by an $S_4$ operation. The symmetry-related angles are C(2)–C(1)–Si–C(1$^a$) and C(12)–C(7)–Si–C(7$^a$), and C(8)–C(7)–Si–C(7$^a$) and C(6)–C(1)–Si–C(1$^a$). In each pair, the values are expected to be of equal magnitude, but oppositely signed. Values for these angles[19] are found to be −56.2, 57.7, −71.0, and 72.1°, respectively. Thus, although **1** lies in a crystallographic site of $C_2$ symmetry and is therefore not constrained to adopt a symmetry higher than $C_2$, the deviation from $S_4$ symmetry is in fact negligible, i.e., less than 2°.

We further note that the values of dihedral angles H(1)–C(1)–Si–C(1$^a$) and H(12)–C(7)–Si–C(7$^a$) are −171.7 and 172.8°, respectively. Thus the cyclohexyl groups are twisted by 7–8° from a $D_{2d}$ conformation.

To determine whether $S_4$ symmetry is also maintained in the isolated molecule, we performed empirical force field (EFF) calculations[20] on **1**. The ground state was found to have

**Table I.** Calculated and Experimental Structural Parameters for Tetracyclohexylsilane

| | X-ray[a] | EFF | |
|---|---|---|---|
| | | $S_4$ | $D_2$ |
| Si-C, Å | 1.914, 1.904 | 1.897 | 1.897 |
| C-$C_{av}$, Å | 1.536 | 1.529 | 1.530 |
| Si-C(1)-C(2), deg | 113.9, 113.6 | 112.2 | 115.0 |
| Si-C(1)-C(6), deg | 116.8, 116.3 | 117.2 | 116.1 |
| C-Si-C, deg[b] | 114.8(1), 114.1(1), 107.3(2), 106.8(2) | 113.4(2), 107.6(4) | 112.1(2), 109.1(2), 107.3(2) |
| C-$C_t$-C, deg[c] | 109.3, 109.2 | 110.7 | 109.2 |
| C(2)-C(1)-Si-C($1^a$), deg | −56.2 | −52.4 | −56.3 |
| C(8)-C(7)-Si-C($7^a$), deg | −71.0 | −78.0 | −56.8 |
| H(1)-C(1)-Si-C($1^a$), deg | −171.7 | −168.4 | 172.0 |
| H(12)-C(7)-Si-C($7^a$), deg | 172.8 | 167.9 | 171.5 |
| rel energy, kcal/mol | | 0.00 | 1.14 |

[a] Reference 17. [b] The value in parentheses gives the number of symmetry-equivalent angles in each set. Note that for $C_2$, $D_2$, and $S_4$ symmetries, there are four, three, and two sets, respectively. [c] $C_t$ = tertiary carbon.

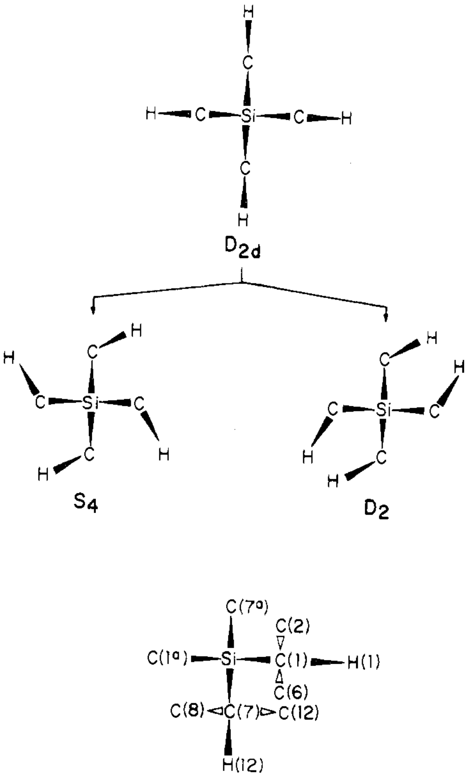

**Figure 1.** Top: partial subgroup lattice for tetracyclohexylsilane (**1**). The relative twists of the cyclohexyl rings are indicated by the methine hydrogens. Bottom: partial numbering scheme for **1**. The solid wedges are related to the stereo formula at the top. The hollow wedges indicate bonds to cyclohexane methylene carbon atoms.

$S_4$ symmetry, with structural parameters in close agreement with the X-ray structure (Table I). A slightly higher energy conformation with $D_2$ symmetry was also found. Input structures with $D_{2d}$ and $C_2$ symmetries relaxed to $S_4$ or $D_2$.[21]

To the best of our knowledge, **1** is the first example of a tetraalkyl group 4A derivative with $S_4$ ground-state symmetry.[22]

**Acknowledgment.** We thank the National Science Foundation (Grant CHE77-07665) for support of this work.

**Registry No.** Tetracyclohexylsilane, 1099-44-1.

## References and Notes

(1) M. G. Hutchings, J. D. Andose, and K. Mislow, *J. Am. Chem. Soc.*, **97**, 4553 (1975).

(2) H. T. Sumsion and D. McLachlan, Jr., *Acta Crystallogr.*, **3**, 217 (1950); A. Robbins, G. A. Jeffrey, J. P. Chesick, J. Donohue, F. A. Cotton, B. A. Frenz, and C. A. Murillo, *Acta Crystallogr., Sect. B*, **31**, 2395 (1975). Although $S_4$ symmetry is unambiguously established for the molecule in the crystal, empirical force field calculations[1] indicate $D_{2d}$ symmetry for the isolated molecule; cf. also D. A. Dougherty and K. Mislow, *J. Am. Chem. Soc.*, in press.

(3) M. Yokoi, *Bull. Chem. Soc. Jpn.*, **30**, 100 (1957); C. Glidewell and G. M. Sheldrick, *J. Chem. Soc. A*, 3127 (1971); P. C. Chieh, *J. Chem. Soc., Dalton Trans.*, 1207 (1972). Empirical force field calculations[1] indicate $S_4$ symmetry for the isolated molecule.

(4) P. C. Chieh, *J. Chem. Soc. A*, 3243 (1971); A. Karipides and D. A. Haller, *Acta Crystallogr., Sect. B*, **28**, 2889 (1972).

(5) P. C. Chieh and J. Trotter, *J. Chem. Soc. A*, 911 (1970); N. A. Akhmed and G. G. Aleksandrov, *J. Struct. Chem.* (*Engl. Transl.*), **11**, 824 (1970).

(6) V. Busetti, M. Mammi, A. Signor, and A. Del Pra, *Inorg. Chim. Acta*, **1**, 424 (1967).

(7) T. L. Khotsyanova and Y. T. Struchkof, *Kristallografiya*, **1**, 669 (1956); P. Goldstein, K. Seff, and K. N. Trueblood, *Acta Crystallogr., Sect B*, **24**, 778 (1968).

(8) J. Bordner and L. D. Freedman, *Phosphorus*, **3**, 33 (1973).

(9) B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957); G. J. Palenik, *Acta Crystallogr.*, **20**, 471 (1966); G. F. Brown and E. I. Stiefel, *Inorg. Chem.*, **12**, 2140 (1973); F. A. Cotton and C. A. Murillo, *ibid.*, **14**, 2467 (1975).

(10) (a) A. Karipides and B. Foerst, *Acta Crystallogr., Sect. B*, **34**, 3494 (1978); (b) A. Karipides, C. Forman, R. H. P. Thomas, and A. T. Reed, *Inorg. Chem.*, **13**, 811 (1974).

(11) A. Karipides and K. Wolfe, *Acta Crystallogr., Sect. B*, **31**, 605 (1975).

(12) N. I. Sadova, N. I. Popik, and L. V. Vilkov, *J. Mol. Struct.*, **31**, 399 (1976).

(13) This is the case when the counterion is unsymmetrical: M. Di Vaira and A. Bianchi Orlandini, *J. Chem. Soc., Dalton Trans.*, 1704 (1972); C. Floriani, F. Calderazzo, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 384 (1973). However, with $K^+$ or $(CH_3)_4N^+$ as counterions, exact $D_{2d}$ symmetry is found: K. Hoffmann and E. Weiss, *J. Organomet. Chem.*, **67**, 221 (1974).

(14) T. Glowiak, R. Grobelny, B. Jezowska-Trezebiatowska, G. Kreisel, W. Seidel, and E. Uhlig, *J. Organomet. Chem.*, **155**, 39 (1978).

(15) A. Karipides and M. Oertel, *Acta Crystallogr., Sect. B*, **33**, 683 (1977).

(16) (a) A. Karipides, A. T. Reed, and R. H. P. Thomas, *Acta Crystallogr., Sect B*, **30**, 1372 (1974); (b) A. Karipides, A. T. Reed, D. A. Haller, and F. Hayes, *ibid.*, **33**, 950 (1977).

(17) A. Karipides, *Inorg. Chem.*, **17**, 2604 (1978).

(18) Another $D_{2d}$ conformation exists in which each cyclohexyl group is twisted by 180° relative to the structure shown in Figure 1. However, molecular models suggest that this structure, and structures with appropriate subsymmetries, are highly hindered, and these conformations are therefore not considered further.

(19) Calculated from the X-ray coordinates reported in ref 17.

(20) The program BIGSTRN is available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47401 (J. D. Andose et al., *QCPE*, **10**, 348 (1978)) and has been previously described. See, for example, W. D. Hounshell, L. D. Iroff, R. J. Wroczynski, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 5212 (1978), and references therein.

(21) An input structure with $D_{2d}$ symmetry ($\phi$(H–C–Si–C) = 180°) relaxed to $S_4$. $C_2$ input structures with $\phi$ values of 160 and 170°, 160 and −170°, and 180 and 170° relaxed to $D_2$, $S_4$, and $S_4$ conformations, respectively.

(22) Empirical force field calculations have shown that compounds of the type $M[C(CH_3)_3]_4$ and $M[Si(CH_3)_3]_4$, where M is an element of group 4A, exist in at least two conformational states: a ground state with *T* symmetry and a higher energy conformer with $S_4$ symmetry (L. D. Iroff and K. Mislow, *J. Am. Chem. Soc.*, **100**, 2121 (1978)).

Department of Chemistry
Miami University
Oxford, Ohio 45056

**Anastas Karipides***

Department of Chemistry
Princeton University
Princeton, New Jersey 08540

**Linda D. Iroff**
**Kurt Mislow***

*Received October 25, 1978*