

potassium bis(triacetonitrilo)nickel(II) octahydrate, K₄Ni[N(CH₂COO)₃]₂·(H₂O)₈, the Ni–N and Ni–O bond distances are 2.12 and 2.06 Å respectively (Fomenko, Polynova, Poray-Koshits & Mitrofanova, 1972). The structure of the bis[2,2'-iminobis(acetamidoxime)]nickel(II) cation in a chloride hydrate (Cullen & Lingafelter, 1970) is very similar in shape and dimensions to our Ni complex, with allowance for the slightly longer distance where Ni–N takes the place of Ni–O, and disregarding a few extra peripheral atoms. Angles in the chelate rings and at Ni agree within 2° on average with the values reported here for corresponding angles.

In the Cs salt, all of the H atoms of water molecules are involved in hydrogen bonds to other O atoms; relevant distances and angles are listed in Table 3. In the Li salt, H(7) and H(9) are well situated for hydrogen bonds, while H(6) may weakly hydrogen-bond (Table 3). In this salt, H(8) has no neighbor suitable for hydrogen bonding.

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References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CULLEN, D. L. & LINGAFELTER, E. C. (1970). *Inorg. Chem.* **9**, 1865–1877.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
 FOMENKO, V. V., POLYNOVA, T. N., PORAY-KOSHITS, M. A. & MITROFANOVA, N. D. (1972). *Zh. Strukt. Khim.* **13**, 343–344.
 KRAMARENKO, F. G., POLYNOVA, T. N., PORAY-KOSHITS, M. A., CHAYLI, V. P. & MITROFANOVA, N. D. (1974). *Zh. Strukt. Khim.* **15**, 161.

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9-Methyl-9-(3-dimethylaminopropyl)-9,10-dihydrosilanthracene Hydrochloride

BY EUGENE R. COREY,* JOYCE Y. COREY AND WILLIAM F. PATON

Department of Chemistry, University of Missouri–St Louis, St Louis, Missouri 63121, USA

AND MILTON D. GLICK

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

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Abstract. C₁₉H₂₆ClNSi, *M_r* = 331.96; monoclinic, *P*2₁/*c*, *a* = 17.207 (4), *b* = 6.915 (2), *c* = 17.066 (4) Å, β = 104.18 (2)°; *Z* = 4, *D_m* = 1.13 (1), *D_c* = 1.12 g cm⁻³, *U* = 1968.8 (9) Å³; μ(Mo *K*α) = 2.54 cm⁻¹. A folded conformation is adopted with a dihedral angle between benzo group planes of 132.1° and an extended dimethylaminopropyl side chain in the pseudoaxial position on the Si hetero-atom.

Introduction. Crystals of the title compound were prepared by J. Y. Corey. The product was purified and recrystallized from xylene–chloroform mixtures.† A crystal 0.3 × 0.3 × 0.2 mm was mounted on a Syntex

*P*2₁ diffractometer and data were collected to 2θ = 52° with Mo *K*α (λ = 0.71069 Å) radiation (graphite monochromator) and the θ–2θ scan technique at 2° min⁻¹. Backgrounds were measured at each end of the scan [2θ scan range: 2θ(Mo *K*α₁) – 1.0° to 2θ(Mo *K*α₂) + 1.0°] for a total time equal to one-half the scan time. Systematic absences were *h*0*l*, *l* odd; 0*k*0, *k* odd, uniquely determining the space group *P*2₁/*c*. Fifteen reflections with 2θ between 20 and 28° were centered with a programmed centering routine; cell parameters were obtained by least-squares refinement of these angles. During data collection, the intensities of three standard reflections were measured every 97 reflections with no significant variation in intensity observed. The data were reduced to *F*² and σ(*F*²) by procedures similar to those described previously (Schmonsees, 1974; Mivake, Togawa & Hosoya, 1964). Standard

* To whom correspondence should be addressed.

† Details of the synthetic procedures will be published at a later date.

deviations were assigned as follows: $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.03I)^2]^{1/2}$, where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background count, and K = ratio of scan time to background time. No corrections for absorption were made. The 2024 data with $F_o^2 > 3\sigma(F_o^2)$ from the 4399 data scanned were used in the structure solution and refinement.

The structure was solved by an iterative application of the Σ_2 relationship (Long, 1965; Sayre, 1952) with 199 normalized structure factors of magnitude 1.3 or greater. An E map based on the set of phases for the solution with the largest consistency index (0.977) gave the positions of the atoms for the major part of the structure; the additional atoms were located from a difference map. Least-squares refinement (Busing, Martin & Levy, 1962) of the non-H atoms with isotropic thermal parameters gave a discrepancy value $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.118$. Refinement was continued with anisotropic thermal parameters for the non-H atoms and an isotropic thermal parameter for the H bonded to N [the H atoms bonded to C were included in the calculations at ideal locations (Zalkin, 1974) with fixed C—H distances of 1.0 Å and isotropic thermal parameters 10% larger than the equivalent isotropic B of the atom to which they are bonded]. The fixed isotropic B values for the H atoms ranged from 4.1 to 7.5 Å². Table 1 gives the final positional parameters with associated estimated standard deviations for atoms which were refined. Final discrepancy values were $R_1 = 0.046$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2} = 0.049$.*

Table 1. Final positional parameters (10⁴) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	4058 (2)	837 (6)	902 (2)
C(2)	4757 (3)	1744 (8)	873 (2)
C(3)	5049 (3)	3232 (8)	1408 (3)
C(4)	4635 (3)	3776 (6)	1990 (2)
C(5)	3392 (2)	1764 (6)	3944 (2)
C(6)	3151 (3)	252 (8)	4354 (2)
C(7)	2733 (3)	-1272 (7)	3943 (2)
C(8)	2558 (2)	-1318 (6)	3098 (2)
Si(9)	2675 (1)	173 (1)	1549 (1)
C(10)	3489 (2)	3442 (5)	2658 (2)
C(11)	3221 (2)	1750 (5)	3102 (2)
C(12)	2801 (2)	192 (6)	2667 (2)
C(13)	3622 (2)	1358 (5)	1463 (2)
C(14)	3921 (2)	2831 (6)	2018 (2)
C(15)	2585 (2)	-2346 (5)	1139 (2)
C(16)	1792 (2)	1668 (5)	1032 (2)
C(17)	1605 (2)	1575 (5)	105 (2)
C(18)	850 (2)	2709 (5)	-285 (2)
N(19)	522 (2)	2172 (4)	-1155 (2)
C(20)	-311 (2)	2900 (6)	-1460 (2)
C(21)	1041 (2)	2820 (6)	-1683 (2)
Cl(22)	470.5 (7)	-2187 (1)	-1209.0 (6)
H(N19)	499 (18)	670 (52)	-1161 (18)

The largest parameter shift in the final cycle of full-matrix refinement was less than 10% of its standard deviation; the error of fit was 1.69. Atomic scattering factors and real and imaginary anomalous dispersion corrections for Cl and Si were taken from *International Tables for X-ray Crystallography* (1974). The highest residual electron density in the final difference map was 0.29 e Å⁻³.

Discussion. The title compound is one of a group of tricyclic Si heterocycles with central rings of varying sizes which are currently being examined for central nervous system activity (Corey, Corey & Glick, 1976; Paton, Corey, Corey & Glick, 1977). The title compound adopts a folded boat conformation with an extended dimethylaminopropyl side chain occupying the pseudo-axial position on the Si hetero-atom.

The molecule and the numbering scheme are shown in Fig. 1 (Johnson, 1965). Table 2 gives the values of the interatomic bond lengths and angles (Busing, Martin & Levy, 1964). The dihedral angle between the least-squares benzo group planes is 132.1°.

Table 3 presents a tabulation of benzo group dihedral angles for dihydroanthracenes with atoms at the 9

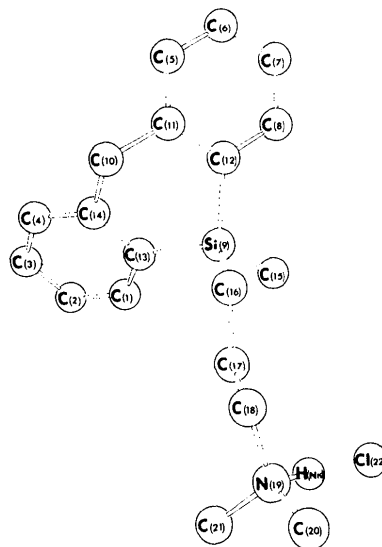


Fig. 1. Atom numbering for the title compound.

* A list of structure factors and tables of thermal parameters, positional parameters for the H atoms, torsion angles about the central ring and the 3-dimethylaminopropyl side chain, a packing diagram, and least-squares planes for the benzo groups and the central ring have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32272 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and 10 positions which are bonded to four other atoms (*i.e.* two tetravalent atoms). The first group of compounds consists of carbocycles which display the following trends: placement of one or two substituents in the axial position(s) results in an increase in the value of the dihedral angle relative to the parent carbocycle; a substituent in an equatorial position apparently results in a decrease in the dihedral angle; replacement of a CHR group in the 10 position by a second short-period tetravalent hetero-atom results in a decrease in the dihedral angle between benzo groups. Reports of X-ray

structural studies of dihydroanthracenes with second-period hetero-atoms in both the 9 and 10 positions indicate that tetravalent S atoms may result in a further decrease of the dihedral angle (diphenylene disulphone $\sim 127^\circ$, Hosoya, 1958) but that tetravalent Si increases the dihedral angle (9,10-disiladihydroanthracene 156° , D'yachenko, Atovmyan & Soboleva, 1975; 9,9,10,10-tetramethyl-9,10-disiladihydroanthracene 156° , D'yachenko *et al.*, 1974; 9,9,10,10-tetraphenyl-9,10-disiladihydroanthracene 180° , Soboleva, D'yachenko & Atovmyan, 1974).

Table 2. Bond lengths (Å) and angles ($^\circ$)

C(1)–C(2)	1.369 (5)	Si(9)–C(12)	1.867 (3)	C(5)–C(6)	1.377 (6)	C(10)–C(11)	1.526 (5)
C(2)–C(3)	1.386 (6)	Si(9)–C(13)	1.861 (4)	C(6)–C(7)	1.369 (6)	C(10)–C(14)	1.524 (5)
C(3)–C(4)	1.409 (6)	Si(9)–C(15)	1.869 (4)	C(7)–C(8)	1.399 (5)	C(16)–C(17)	1.537 (4)
C(4)–C(14)	1.402 (5)	Si(9)–C(16)	1.871 (4)	C(8)–C(12)	1.399 (5)	C(17)–C(18)	1.524 (5)
C(13)–C(14)	1.400 (5)	N(19)–C(20)	1.488 (4)	C(11)–C(12)	1.404 (5)	C(18)–N(19)	1.501 (4)
C(1)–C(13)	1.400 (5)	N(19)–C(21)	1.484 (4)	C(5)–C(11)	1.395 (4)	N(19)–H(N19)	1.04 (3)
C(1)–C(2)–C(3)	119.8 (4)	C(12)–Si(9)–C(16)	110.8 (2)	C(5)–C(11)–C(10)	119.6 (3)		
C(2)–C(3)–C(4)	119.9 (4)	C(13)–Si(9)–C(15)	112.0 (2)	C(8)–C(12)–Si(9)	123.9 (3)		
C(3)–C(4)–C(14)	119.9 (4)	C(13)–Si(9)–C(16)	110.2 (2)	C(10)–C(11)–C(12)	120.3 (3)		
C(4)–C(14)–C(13)	119.7 (4)	C(15)–Si(9)–C(16)	110.8 (2)	C(11)–C(12)–Si(9)	117.5 (3)		
C(14)–C(13)–C(1)	118.7 (3)	C(20)–N(19)–H(N19)	108 (2)	C(11)–C(10)–C(14)	113.8 (3)		
C(13)–C(1)–C(2)	122.0 (4)	C(21)–N(19)–H(N19)	109 (2)	Si(9)–C(16)–C(17)	113.8 (2)		
C(4)–C(14)–C(10)	118.7 (4)	C(5)–C(6)–C(7)	120.7 (4)	C(16)–C(17)–C(18)	111.6 (3)		
C(1)–C(13)–Si(9)	124.5 (3)	C(6)–C(7)–C(8)	120.0 (4)	C(17)–C(18)–N(19)	112.2 (3)		
C(10)–C(14)–C(13)	121.6 (3)	C(7)–C(8)–C(12)	120.5 (4)	C(18)–N(19)–C(20)	111.0 (3)		
C(14)–C(13)–Si(9)	116.8 (3)	C(8)–C(12)–C(11)	118.4 (3)	C(18)–N(19)–C(21)	113.0 (3)		
C(12)–Si(9)–C(13)	101.1 (2)	C(12)–C(11)–C(5)	120.1 (4)	C(18)–N(19)–H(N19)	105 (2)		
C(12)–Si(9)–C(15)	111.5 (2)	C(11)–C(5)–C(6)	120.3 (4)	C(20)–N(19)–C(21)	110.9 (3)		

Table 3. Benzo group dihedral angles for dihydroanthracene derivatives with tetravalent atoms in the 9 and 10 positions

	R	R'	Dihedral angle ($^\circ$)	Reference
	H	H	$\sim 145^{(a)}$	Ferrier & Iball (1954)
	H	C(CH ₃) ₃ ^(b)	147	Brennan, Putkey & Sundaralingam (1971)
	CH ₃ ^(b)	C ₂ H ₅ ^(b)	152	Bordner, Stanford & Zieger (1973)
	CH ₃ ^(b)	(CH ₂) ₃ N(CH ₃) ₂ .HCl.H ₂ O.C ₃ H ₆ O ^(b,c,d)	155.6 155.7	Chu & Chung (1976)
	CH ₃ ^(e)	CH(CH ₃) ₂ ^(b)	129	Stanford (1973)
	H	–	133.9	Chu & Chung (1974)
	CH ₂ C ₆ H ₁₁ ^(b)	–	133.7	Chu & Mangion (1975)
	CH ₂ CH(CH ₃) ₂	–	141.8	Chu & Chung (1973)
	H	H	136	D'yachenko, Atovmyan & Soboleva (1976)
	CH ₃ ^(e)	(CH ₂) ₃ N(CH ₃) ₂ .HCl ^(b)	132.1	This work

(a) Two dimensional structure. (b) Axial substituent. (c) Two molecules per asymmetric unit. (d) CF₃ substituent at position 2 of tricyclic. (e) Equatorial substituent.

In the solid state, the *trans-trans* and *trans-gauche* configurations for the C_α-C_β and C_β-C_γ bonds of the dimethylaminopropyl substituent have been observed (Corey, Corey & Glick, 1976). The dimethylaminopropyl groups of the two independent molecules in the recently published structure of (+)-*cis*-9-(3-dimethylaminopropyl)-10-methyl-2-(trifluoromethyl)-9,10-dihydroanthracene (Chu & Chung, 1976) have the *trans-trans* configuration, as is observed in this structure.

The distance between the chloride ion and the quarternary ammonium center is 3.016 (3) Å; the Cl to H distance in the hydrogen bond is 1.98 (4) Å and the N-H...Cl angle is 178 (3)°. The closest intermolecular nonbonded distance between non-H atoms is 3.641 (4) Å between Cl(22) and C(20)', related by translation in the y direction.

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References

- BORDNER, J., STANFORD, R. H. JR & ZIEGER, H. E. (1973). *Acta Cryst.* **B29**, 313-318.
- BRENNAN, T., PUTKEY, E. F. & SUNDARALINGAM, M. (1971). *J. Chem. Soc. (D)*, pp. 1490-1491.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
- CHU, S. S. C. & CHUNG, B. (1973). *Acta Cryst.* **B29**, 2253-2259.
- CHU, S. S. C. & CHUNG, B. (1974). *Acta Cryst.* **B30**, 1616-1618.
- CHU, S. S. C. & CHUNG, B. (1976). *Acta Cryst.* **B32**, 836-842.
- CHU, S. S. C. & MANGION, M. (1975). *Acta Cryst.* **B31**, 2134-2136.
- COREY, E. R., COREY, J. Y. & GLICK, M. D. (1976). *Acta Cryst.* **B32**, 2025-2031.
- D'YACHENKO, O. A., ATOVMIAN, L. O. & SOBELEVA, S. V. (1975). *Zh. Strukt. Khim.* **16**, 505-508; *Chem. Abs.* **83**, 200520i.
- D'YACHENKO, O. A., ATOVMIAN, L. O. & SOBOLEVA, S. V. (1976). *Zh. Strukt. Khim.* **16**, 191-193; *Chem. Abs.* **84**, 179557w.
- D'YACHENKO, O. A., ATOVMIAN, L. O., SOBOLEVA, S. V., MARKOVA, T. YU., KOMALENKOVA, N. G., SHAMSHIN, L. N. & CHERNYSHEV, E. A. (1974). *Zh. Strukt. Khim.* **15**, 170-171; *Chem. Abs.* **80**, 125760f.
- FERRIER, W. G. & IBALL, J. (1954). *Chem. Ind.* pp. 1296-1297.
- HOSOYA, S. (1958). *Chem. Ind.* pp. 980-981.
- HOSOYA, S. (1966). *Acta Cryst.* **21**, 21-26.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- LONG, R. E. (1965). *The Crystal and Molecular Structures of 7,7,8,8-Tetracyanoquinodimethane and Cyclopropane-carboxamide and a Program for Phase Determination*, Thesis, Appendix III, Univ. of California, Los Angeles.
- MIYAKE, S., TOGAWA, S. & HOSOYA, S. (1964). *Acta Cryst.* **17**, 1083-1084.
- PATON, W. F., COREY, E. R., COREY, J. Y. & GLICK, M. D. (1977). *Acta Cryst.* **B33**, 226-228.
- SAYRE, R. (1952). *Acta Cryst.* **5**, 60-65.
- SCHMONSEES, W. (1974). *X-ray Structural Studies of Cobalt and Mercury Transition Metal Complexes*, Thesis, Ch. 1 and Appendix I, Wayne State Univ.
- SOBOLEVA, S. V., D'YACHENKO, O. A. & ATOVMIAN, L. O. (1974). *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1443; *Chem. Abs.* **81**, 112290y.
- STANFORD, R. H. JR (1973). *Acta Cryst.* **B29**, 2849-2855.
- ZALKIN, A. (1974). *HFINDR: A Fortran Program for the Calculation of Idealized Hydrogen Positions*.

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2-Chlorophenoxyacetic Acid

BY K. CHANDRASEKHAR AND VASANTHA PATTABHI

Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600025, India*

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Abstract. C₈H₇O₃Cl, *M_r* = 186.5, monoclinic, space group *P2*₁, *a* = 7.602 (6), *b* = 22.164 (17), *c* = 5.328 (4) Å, β = 114.26 (3)°, *V* = 818.1 Å³, *Z* = 4,

*D*_o = 1.523, *D*_c = 1.514 g cm⁻³. There are two molecules in the asymmetric unit. Strong hydrogen bonds of the O...H-O type are observed.

Introduction. The title compound, a plant-growth hormone, is soluble in warm water, and crystals suitable

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