Table I. Numbers of Catacondensed and Pericondensed Polyhex Graphs and Associated Condensed Polycyclic Aromatic Hydrocarbon Molecular Species[a]

no. of rings	no. of polyhexes[b]	graphite-connected graphs[b]	graphs of nonplanar species	planar molec species	pairs of enantiomers	nonplanar meso compds	total molec species
Catacondensed							
3	2	2	0	2	0	0	2
4	5	5	1	4	1	0	6
5	12	12	4	8	4	0	16
6	37	36	21	16	22	3	63
7	123	118	83	40	104	4	252
8	446	411	354	92	531	10	1164
9	1689	1489	1452	237	2559	21	5376
10	6693	5572	6093	600	12882	47	26411
Pericondensed							
4	1	1	0	1	0	0	1
5	3	3	0	3	0	0	3
6	15	15	4	11	4	0	19
7	72	72	38	34	39	4	116
8	361	353	242	119	287	11	704
9	1824	1734	1432	392	1944	22	4302
10	9332	8535	7977	1355	12454	70	26333

[a] All figures are for systems with Kekulé structures. [b] These enumerations coincide with those obtained previously.[3,7-16]

stereocenter ensures a nonplanar structural moiety. The interplanar four-ring dihedral angle of 30° that is found in benzophenanthrene[28] is typical of the smallest nonplanar structural adjustments characterizing these molecular systems.

The reults obtained for the numbers of stable PAH stereochemical structural isomers have been verified by using molecular mechanics[38] and AM1[39] calculations for all possible chiral and planar structures through six rings,[40] and for over 30 selected examples of stereochemical pairs with seven to nine rings. Each stereoisomer examined is at a well-defined molecular mechanics energy minimum, and the most stable calculated nonplanar geometry always corresponds closely to the experimental X-ray structure (if known). In addition, the molecular mechanics calculations have also been shown to correlate the relatively sparse (11 compounds[41,42]) experimental ΔH_f° data for PAH structures with an average deviation of 1.1 kcal/mol.[40]

An intriguing aspect of the present work is the understanding that a *majority* of polycyclic benzenoids capable of existence will have highly nonplanar molecular structures. The planar polycyclic aromatics are therefore the unusual systems, since the planar molecules comprise only a small fraction of the potential realizable compounds.

The computerized examination of the structure code data used for this work also gives a detailed analysis of several types of other structural features (e.g., 1,2 and 1,4 addition reaction sites, bay regions, and fjord regions). The complete results of this finer delineation of molecular structure for the PAHs and extensions to larger systems will be presented in a complete paper.

Coordination Geometry of Gaseous Hexamethyltungsten: Not Octahedral

Arne Haaland,* Andreas Hammel,[†] Kristin Rypdal, and Hans V. Volden

Department of Chemistry, University of Oslo Box 1033, Blindern, 0315 Oslo 3, Norway

Wang, Albright, and Eisenstein[1] have shown that d⁰ ML_6 complexes may prefer a trigonal-prismatic D_{3h} coordination geometry to the ubiquitous octahedral O_h configuration: ab initio molecular orbital calculations on the model compounds TiH_6^{2-} and CrH_6 with large, better than double ζ bases and electron correlation included at the fourth-order Møller-Plesset level indicate that the energy of the trigonal-prismatic configuration of TiH_6^{2-} is 9.2 kcal mol⁻¹ lower than that of the octahedral. The calculations on CrH_6 indicate that the energy of the prismatic configuration is 157 kcal mol⁻¹ lower than that of the octahedral, and further lowering of the symmetry from D_{3h} to C_{3v} reduces the energy by another 17.5 kcal mol⁻¹. Wang, Albright, and Eisenstein concluded that a trigonal-prismatic D_{3h} or C_{3v} configuration of d⁰ ML_6 complexes is favored when M-L bonding is strong and nonpolar and when the ligand is not bulky and has little or no π-donating capability.

Very recently, Morse and Girolami[2] have reported the crystal structure of [Li(tmeda)]₂[ZrMe₆], tmeda = N,N,N',N'-tetramethylethylenediamine, Me = CH_3. The [ZrMe₆]²⁻ anion is, of course, pseudoisoelectronic with TiH_6^{2-} and was indeed found to

(31) Muir, K. W.; Robertson, J. M. *Acta Crystallogr.* **1971**, *B28*, 879.
(32) Kohno, Y.; Konno, M.; Saito, Y.; Inokuchi, H. *Acta Crystallogr.* **1975**, *B31*, 2076.
(33) Oonishi, I.; Fujisawa, S.; Aoki, J.; Danno, T. *Bull. Chem. Soc. Jpn.* **1977**, *51*, 2256.
(34) Herbstein, F. H. *Acta Crystallogr.* **1979**, *B35*, 1661.
(35) Fujisawa, S.; Oonishi, I.; Aoki, J.; Ohashi, Y.; Sasada, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3424.
(36) Oonishi, I.; Fujisawa, S.; Aoki, J.; Ohashi, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2233.
(37) For leading references to the structures of planar catacondensed PAHs, see: Herndon, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 7605.
(38) For a review, see: Burkett, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982. The program used in this work (PCMODEL Version 3) is available from Serena Software, Box 3076, Bloomington, IN 47402.
(39) Dewar, M. J. S.; Stewart, J. J. P.; Egger, M. Program No. 527, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47401. Also see: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(40) Herndon, W. C.; Connor, D. A.; Lin, P. *Pure Appl. Chem.* **1990**, *62*, 435.
(41) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.
(42) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.
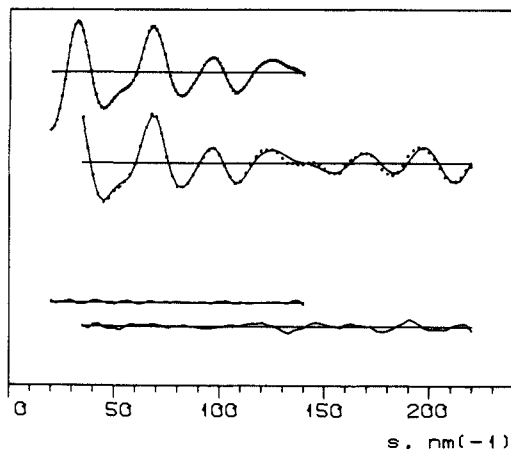
† Present address: Institute for Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Germany.

(1) Wang, S. K.; Albright, T. A.; Eisenstein, O. *Inorg. Chem.* **1989**, *28*, 1611-1613.
(2) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 4114-4116.

Figure 1. Experimental (●) and calculated (—) modified molecular intensity curves for WMe₆. Below: difference curves.
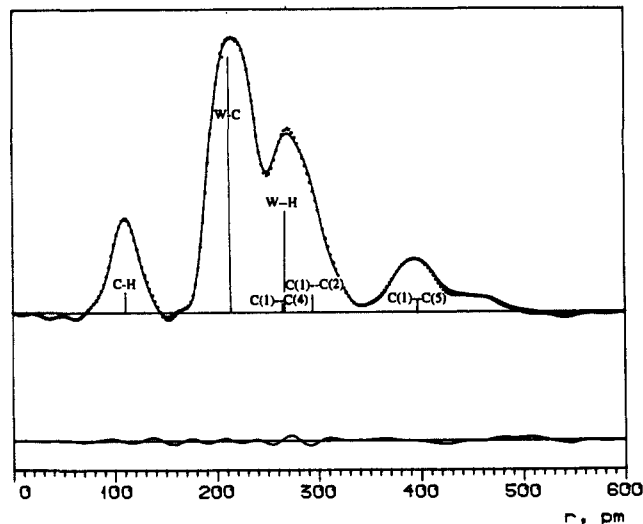

Figure 2. Experimental (●) and calculated (—) radial distribution curves for WMe₆. Artificial damping constant $k = 0.004$ Å².

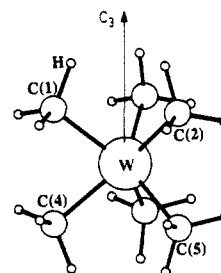**Figure 3.** Molecular model of WMe₆. Symmetry D_{3h}.

possess the trigonal-prismatic configuration. Since each of the two (tmeda)Li⁺ fragments bridge two methyl groups in the same triangular face, it appears unlikely that the configuration of the anion is determined by interionic interactions.

We now report the molecular structure of hexamethyltungsten as determined by gas-phase electron diffraction. The molecule which is pseudoisoelectronic with CrH₆ is found to possess a trigonal-prismatic coordination geometry.

Hexamethyltungsten, first prepared by Wilkinson and co-workers,[3] is air-sensitive, decomposes at temperatures above −40 °C, and may detonate in vacuum. Following Galyer and Wilkinson,[3b] we prepared WMe₆ from WCl₆ and 6 molar equiv of AlMe₃ in isopentane. Galyer and Wilkinson removed the by-product AlMe₂Cl by adding trimethylamine. We found that addition of the amine, removal of the solid adduct Me₃NAlMe₂Cl, and subsequent sublimation yielded a product contaminated by an orange compound containing W and N. (This compound may have been formed by reaction between WMe₆ and NHMe₂ present as an impurity in our amine.) We therefore crystallized WMe₆ directly from the concentrated reaction mixture at −90 °C. The dark red crystals thus obtained still contained considerable amounts of AlMe₂Cl. This impurity, which is more volatile than WMe₆, was removed during the subsequent sublimation from about −5 °C into a U-tube at −20 °C. Though this procedure led to considerable loss of product, it yielded blood-red WMe₆ of high purity. The 300-MHz ¹H NMR spectrum in toluene-*d₈* at 20 °C consisted of a singlet at $\delta = 1.78$ ppm with satellites due to ¹⁸³W–H coupling; $J(^{183}\text{W–H}) = 6$ Hz. The decoupled 75.430-MHz ¹³C NMR spectrum consisted of a singlet at $\delta = 83.11$ ppm with satellites due to ¹⁸³W–¹³C coupling; $J(^{183}\text{W–}^{13}\text{C}) = 43.3$ Hz.

The electron diffraction data were recorded on Balzers Eldigraph KDG-2 instrument with an all-glass inlet system. A sample reservoir containing 2 or 3 g of WMe₆ was connected to the inlet system through a valve. In order to avoid detonations, the reservoir was kept at temperatures between −10 and 0 °C and small amounts of material, sufficient for the exposure of *one* plate, sublimed into the inlet system and condensed at dry ice temperatures. The valve was then closed, the reservoir cooled to about −30 °C, and the diffraction data recorded one plate at a time as the inlet system reached room temperature. A mass spectrum recorded in the same manner gave no indication of decomposition during our experiment.

Structure refinements were based on data from six plates exposed with a nozzle-to-plate distance of 50 cm and covering the scattering range $s = 2.00–14.00$ Å⁻¹ with increment $\Delta s = 0.125$ Å⁻¹ and from four plates exposed with a nozzle-to-plate distance of 25 cm and covering the scattering range $s = 3.50–22.00$ Å⁻¹ with increment $\Delta s = 0.25$ Å⁻¹. The diffraction pattern was re-

producible from plate to plate: Average standard deviations of modified molecular intensities (relative to the mean) ranged from 0.8 to 1.6% for the 50-cm plates and from 2.9 to 3.9% for the 25-cm plates. Atomic scattering factors were taken from ref 4. Experimental modified molecular intensity curves are displayed in Figure 1. Three-atom scattering was included when the theoretical counterparts were calculated.

A radial distribution curve calculated by Fourier inversion of the experimental molecular intensity is shown in Figure 2. The peak centered at $r = 2.15$ Å represents the W–C bond distances. The vibrational amplitude of the W–C bond obtained by least-squares refinement of a D_{3h} model (see below), $l = 0.060$ (3) Å, shows that W–C distances are equal or very nearly so; individual bond distances cannot differ from their mean by more than a few hundredths of an angstrom. If WMe₆ were octahedral, the radial distribution (RD) curve should contain a peak at 4.30 Å representing *three* nonbonded trans C--C distances and a peak at 3.04 Å, possibly not resolved from the W--H peak at about 2.70 Å, representing 12 nonbonded cis C--C distances. Inspection of the experimental RD curve shows that an octahedral coordination geometry is inconsistent with the experimental data: instead of a peak at 4.30 Å, the curve contains a peak at 3.95 Å of area corresponding to *six* C--C distances; the remaining nine C--C distances form a compound peak with the W--H distances at about 2.70 Å.

A trigonal-prismatic model of D_{3h} symmetry as indicated in Figure 3 is determined by four structure parameters: the W–C bond distance; the angle between the W–C(1) bond and the 3-fold symmetry axis, which we denote by θ; the C–H bond distance; and the ∠WCH valence angle. It may be noted that the W–C bond distance and the position of the peak at 3.95 Å are sufficient to fix θ and hence the structure of the WC₆ fragment. Least-

(3) (a) Shortland, A. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1973, 872–876. (b) Galyer, A. L.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1976, 2235–2238.

(4) Bonham, R. A.; Schäfer, L. Complex Scattering Factors for the Diffraction of Electrons by Gases. In *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, 1974; Vol. IV, pp 176–272.

Table I. Internuclear Distances, Vibrational Amplitudes (*l*), and Valence Angles of WMe$_6$[a]

	r_a, Å	*l*, Å	angles, deg
W–C	2.146 (3)	0.060 (3)	
C–H	1.119 (4)	0.078 (5)	
W--H	2.682 (8)	0.151 (18)	
C(1)--C(2)	2.928 (12)	[0.17][b]	
C(1)--C(4)	2.645 (16)	[0.13][b]	
C(1)--C(5)	3.946 (5)	0.161 (12)	
θ[c]			52.0 (3)
∠C(1)WC(2)			86.0 (2)
∠C(1)WC(4)			76.1 (6)
∠WCH			106.1 (7)
R[d]		4.7%	

[a] Molecular symmetry D_{3h}. Estimated standard deviations in parentheses in units of the last digit. [b] See comments in text. [c] The angle between the W–C(1) bond and the 3-fold symmetry axis. [d] $R = [\sum w(I_{obsd} - I_{calcd})^2 / \sum w I_{obsd}^2]^{1/2}$.

squares refinement of the four structure parameters along with four root-mean-square vibrational amplitudes yielded the best values listed in Table I. When attempts were made to refine the vibrational amplitudes of the C(1)--C(2) and C(1)--C(4) distances, the refinements failed to converge. These amplitudes were therefore determined by trial and error. Comparison of experimental and calculated intensity and RD curves, Figures 1 and 2, shows that the agreement is satisfactory.

If the symmetry of our model is lowered to C_{3v}, two more adjustable parameters have to be included in the refinements, e.g., a second, symmetry-independent W–C bond distance and a second, symmetry-independent angle θ_2. Such a model would obviously be equally compatible with our data. *We conclude, therefore, that the coordination geometry of hexamethyltungsten is trigonal-prismatic D_{3h} or slightly deformed to C_{3v} symmetry.* WMe$_6$ is, to the best of our knowledge, the first electrically neutral molecule with monodentate ligands that has been found to violate the valence shell electron pair repulsion tenet that the coordination geometry in a molecule of type ML$_6$ where the metal is surrounded by six bonding electron pairs (and no nonbonding electrons) is octahedral.

W(NMe$_2$)$_6$,[5] W(OMe)$_6$,[6] and WF$_6$[7] all have octahedral coordination geometries in the gas phase with W–N = 2.035 (5) Å, W–O = 1.902 (3) Å, and W–F = 1.832 (3) Å. All these bonds are more polar than the W–C bond in WMe$_6$, and all the ligands have at least some π-donor capability. Like the other compounds mentioned above, W(CO)$_6$ is octahedral in the gas phase.[8] W(CO)$_6$, of course, is a d^6 rather than a d^0 complex, and the six d electrons occupy t$_{2g}$ orbitals which have the right symmetry for donation into ligand π* orbitals. The six W–C bonds are therefore shorter, 2.059 (3) Å,[8] and stronger than in the hexamethyl analogue: the mean bond disruption enthalpies are 43.0 and 38.5 kcal mol⁻¹, respectively.[9]

Acknowledgment. We are grateful to the Norwegian Research Council for Science and the Humanities (NAVF) and the VISTA Program for general support and to the NAVF for a scholarship to A.H.

Note Added in Proof. Professor T. A. Albright has informed us that geometry optimization of WMe$_6$ at the ab initio level with a standard effective core potential and a double-ζ basis for the 5s, 5p, 5d, 6s, and 6p orbitals for W and 3-21 and STO-3G bases for C and H yields a *global* minumum of D_{3h} symmetry, W–C

= 2.161 Å, C–H = 1.095 Å (mean value), ∠CWH = 111.1° (mean value), and θ = 51.0°. The energy of the prismatic configuration is 73 kcal mol⁻¹ below the energy of the octahedral configuration at the Hartree–Fock level and 83 kcal mol⁻¹ lower at the MP2 level.

Fischer Route to Pyrido[3,2-*g*]indoles. A Novel Receptor for Urea Derivatives

Vidyadhar Hegde, Puttannachetty Madhukar, Jeffry D. Madura, and Randolph P. Thummel*

Department of Chemistry, University of Houston Houston, Texas 77204-5641

Received July 19, 1989

Recently we have demonstrated the utility of the Fischer indole synthesis in the conversion of phenylhydrazones of α-keto-2,3-cycloalkenopyridines to 3,3'-polymethylene-bridged derivatives of 2-(2'-pyridyl)indole.[1] This same procedure applied to the appropriate diketones also leads to bis-annelated derivatives of 2,6-di(2'-indolyl)pyridine or 3,3'-bridged 2,2'-biindoles.[1,2] These systems have been shown to undergo facile cyclopalladation to provide a metallocycle involving the indole nitrogen. In hopes of extending the utility of these molecules as hosts for other species, we have elaborated our synthetic approach to include pyrido-fused indole derivatives.
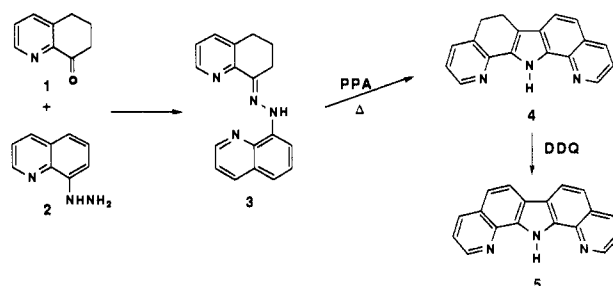
The prerequisite hydrazine is 8-quinolinylhydrazine (2), which can be prepared by stannous chloride reduction of the diazo derivative of 8-aminoquinoline.[3] This hydrazine condenses readily with 5,6,7,8-tetrahydro-8-quinolone (1)[4] to provide the corresponding hydrazone 3. When 3 is heated to 100 °C in polyphosphoric acid (PPA), Fischer cyclization occurs to provide the pyrido[3,2-*g*]indole 4 in 96% yield. If this material is in turn treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a 99% yield of the symmetrical, fully aromatized dipyridocarbazole 5 can be obtained.

In earlier work involving the phenylhydrazones of cyclic 1,2-diketones, it was found that the desired 2,2'-biindoles were contaminated by significant amounts of monoketones, indicating that only one Fischer cyclization had occurred.[1,2] For the bis(hydrazone) derived from the reaction of 1,2-cyclooctanedione with 2, a similar problem was encountered affording a mixture of 7 and 8. Recrystallization from ethanol provided pure 7 (68%).
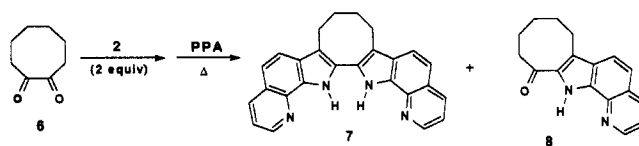
(5) Hagen, K.; Holwill, C. J.; Rice, D. A.; Runnacles, J. D. *Acta Chem. Scand.* **1988**, *A42*, 578–583.
(6) Haaland, A.; Rypdal, K.; Volden, H. V.; Jacob, E.; Weidlein, J. *Acta Chem. Scand.* **1989**, *43*, 911–913.
(7) Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1966**, *20*, 2698–2710.
(8) Arnesen, S. P.; Seip, H. M. *Acta Chem. Scand.* **1966**, *20*, 2711–2727.
(9) Pilcher, G.; Skinner, H. A. Thermochemistry of Organometallic Compunds. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley & Sons: Chichester, 1983; pp 43–90.

(1) Thummel, R. P.; Hedge, V. *J. Org. Chem.* **1989**, *54*, 1720.
(2) (a) Bergman, J.; Pelcman, B. *J. Org. Chem.* **1989**, *54*, 824. (b) Moldenhauer, W.; Simon, H. *Chem. Ber.* **1969**, *102*, 1198. (c) Mann, F. G.; Willcox, T. J. *J. Chem. Soc.* **1958**, 1525.
(3) Buu-Hoï, N. P.; Pèrin, F.; Jacquignon, P. *J. Chem. Soc.* **1960**, 4500.
(4) Thummel, R. P.; Lefoulon, F.; Cantu, D.; Mahadevan, R. *J. Org. Chem.* **1984**, *49*, 2208.