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Theoretical Study and X-ray Structure Determination of Dimethyldihydropyrene

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The dihydropyrene nucleus has an almost planar and completely delocalized 14π electron periphery. In addition, the internal groups are ideally situated for NMR studies, making this system an excellent "probe for aromaticity".[1] Consequently, numerous investigations, both theoretical and experimental, have been carried out on modified dihydropyrenes in order to study the effect of that particular perturbation on the cyclic delocalization (aromaticity) of these systems.[1] There are a few reports in the literature indicating that semiempirical calculations using the AM1 method[2] do not give the correct geometry for the dihydropyrene nucleus.[1b,3] These calculations resulted in a bond-alternating rather than bond-equalized periphery. In general, we have found that the AM1 method leads to excellent results, in good agreement with experiment and higher levels of theory.[4,5] However, in studying cyclically delocalized systems using either semiempirical or ab initio methods, it is well-recognized that the SCF level of theory is not an adequate representation and that, at the least, minimal electron correlation must be introduced.[1b,5,6] With this in mind, we reinvestigated dimethyldihydropyrene (**1**) using the AM1 method as implemented in MOPAC 93.[7]

Initial geometry optimization at the SCF level led to the previously reported[3c] bond-alternating structure **1a** (Table 1). Repeating the SCF calculations with an arbitrary bond-equalized starting geometry, and imposing symmetry during optimization, resulted in a reasonable bond-equalized starting geometry for further study. Lifting the symmetry constraints and reoptimizing, still at the SCF level, resulted in the bond-equalized structure **1b** (Table 1). As can be seen from Table 1, the heat of formation of **1b** is greater than that of **1a**, *at the SCF level*. The two highest occupied orbitals in both **1a** and **1b** are of quite similar energy. Therefore, both orbitals were included in the subsequent reoptimization incorporating electron correlation. Configuration interaction (CI) calculations were performed using a 4 × 4 CI (CI4) that was based on closed-shell SCF orbitals. The MOPAC suite of programs carries out full CI calculations by forming all possible microstates by permuting the electrons among the orbital subspace.[8] The CI4 calculation contains 36 states (20 singlets, 15 triplets, and one quintet). CI4 optimizations of **1a** and **1b** changed the geometries only slightly; however, the heats of formation decreased significantly, particularly in the case of **1b** (Table 1). Although, at the CI4 correlated level of theory, **1b** (in agreement with experiment) is the low energy form, it is apparent that the potential well is very flat and there is little difference in energy between **1a** and **1b** using AM1 CI4. It is interesting to note in the high-order RHF ab initio studies of Siegel et al.[1b] on **1** that **1a** is calculated to be 10 kcal mol^{-1} more stable than **1b** just as in our AM1 (SCF) calculations (AM1 (SCF) ΔE **1b**−**1a** = 9.97 kcal mol^{-1}). Only when electron correlation (MP2) was incorporated in these ab initio calculations was the "correct" C_{2h} bond-equalized geometry (**1b**) obtained.[1b] The agreement between our AM1 (CI4) (~1.396 Å), our experimental X-ray (~1.391 Å), and the density functional theory[1b] (1.409 Å) peripheral bond lengths is most gratifying.

To extend our studies and to once more demonstrate the preeminent importance of electron correlation, a low-level ab initio investigation of **1**, using GAMESS,[9] was carried out. This study was not designed to yield the optimal results available from high-order ab initio and density functional theory (DFT) studies such as those by Siegel et al.[1b] Instead, our goal was to illustrate that the "correct" (bond-equalized) geometry is obtained upon the inclusion of electron correlation even when using a computationally less expensive restricted basis set. Using a 3-21G basis set SCF optimization of **1** again resulted in a bond-alternating structure **1a**. Reoptimizing **1a** employing electron correlation using second-order Møller−Plesset perturbation theory (MP2)[10] or (4,4) MCSCF[11] gave the result we predicted. The MP2- and MCSCF-optimized structures (arrived at directly from **1a** without the imposition of any symmetry constraints) is the bond-equalized **1b**. There is a large drop in energy from **1a** (SCF) and **1a** (MP2 single point) to **1b** (MP2 or MCSCF), Table 1.

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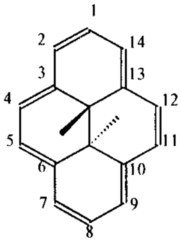
Table 1. Calculated and X-ray Bond Lengths for 1



1

	1a			1b				X-ray Data		
									Present Work	
	AM1/SCF	AM1/CI4	3-21G/SCF [3-21G (MP2)][a]	AM1/SCF	AM1/CI4	3-21G/MP2 [3-21G/SCF][a]	3-21G/MCSCF [3-21G/SCF][a]	ref 12	molecule A	molecule B
Energy[b]	104.5943	97.6930	−687.0374 [−688.6342][a]	114.7910	97.1510	−688.6641 [−687.0148][a]	−687.0626 [−687.0251][a]			
Bond[c] 1−2	1.3521	1.3643	1.337	1.3894	1.3961	1.4107	1.3897	1.390	1.392	1.396
2−3	1.4445	1.4289	1.447	1.3970	1.3962	1.4028	1.3816	1.390	1.389	1.390
3−4	1.3578	1.3707	1.339	1.3985	1.3962	1.4102	1.3904	1.397	1.398	1.397
4−5	1.4430	1.4255	1.453	1.3937	1.3961	1.4073	1.3868	1.392	1.392	1.390
5−6	1.3578	1.3707	1.339	1.3989	1.3967	1.4103	1.3904	1.379	1.397	1.393
6−7	1.4445	1.4278	1.448	1.3970	1.3961	1.4028	1.3815	1.390	1.390	1.389
7−8	1.3521	1.3638	1.337	1.3896	1.3953	1.4109	1.3897	1.354[d]	1.390	1.388
8−9	1.4407	1.4257	1.454	1.3960	1.3961	1.4107	1.3899	1.395	1.392	1.396
9−10	1.3545	1.3667	1.334	1.3911	1.3962	1.4028	1.3815	1.393	1.389	1.390
10−11	1.4494	1.4338	1.454	1.4056	1.3961	1.4102	1.3907	1.393	1.398	1.397
11−12	1.3499	1.3621	1.337	1.3876	1.3962	1.4074	1.3867	1.377	1.392	1.390
12−13	1.4494	1.4345	1.454	1.4058	1.3970	1.4103	1.3907	1.379	1.397	1.393
13−14	1.3545	1.3654	1.334	1.3826	1.3926	1.4028	1.3815	1.390	1.390	1.389
14−1	1.4407	1.4264	1.454	1.3971	1.3943	1.4107	1.3899	1.354[d]	1.390	1.388

[a] Single-point calculation. [b] Energy, AM1 Heat of formation (kcal mol^{-1}), 3-21G total energy (hartree). [c] Bond lengths (Å). [d] This unusually short bond length is probably an artifact of the ambient temperature X-ray experiment.

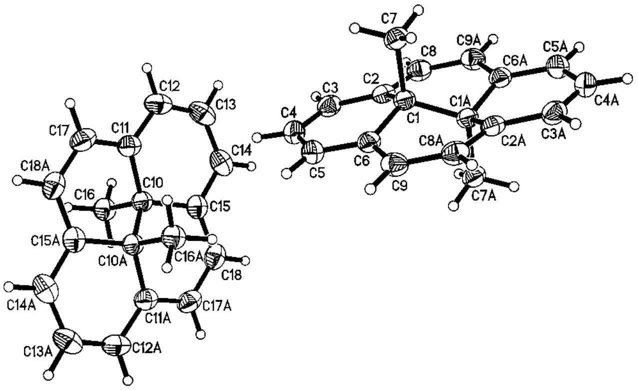


Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids drawn at 50% probability level.

X-ray of Dimethyldihydropyrene

There are only three previous reports of X-ray structures on the dihydropyrene nucleus.[12−14] A recent X-ray structure determination of the parent **1** was carried out at ambient temperature.[12] Unfortunately, the structure was difficult to refine and not all atoms were clearly defined. In this study, the crystallographic data was obtained at 173(2) K, which resulted in a better refinement and a structure (Figure 1) in which all of the aromatic C−C bonds are essentially of equal length. As previously reported,[12] the unit cell contains two crystallographically independent molecules, each of which contain symmetry-generated equivalent atoms. In molecule A, this operation is $-x + 2, -y + 3, -z + 1$, whereas in molecule B the corresponding operation is $-x + 2, -y + 2, -z$. These two molecules lie almost normal to each other at 78.32(3)°. A least-squares plane analysis of the peripheral carbon atoms shows that they are almost coplanar. For molecule A, this plane is described by the equation $2.719(3)x - 4.920(3)y + 7.683(5)z = 6.228(8)$ with a mean plane deviation of 0.028(1) Å. The carbon atoms (X-ray numbering) C2 and C6 show a maximum deviation of 0.038(1) and 0.045(1) Å below the plane and their symmetry equivalent atoms C2A and C6A an equal deviation above the plane. The internal carbon atoms C1/C1A and C7/C7A are ±0.3602(1) and ±1.9148(1) Å above and below the plane containing the peripheral "aromatic" carbon atoms. Correspondingly, the equation of plane in molecule B is $5.426(3)x + 2.933(3)y + 10.000(4)z = 8.353(3)$ with a mean plane deviation of 0.027(1) Å. The maximum deviation is shown by the carbon atoms (X-ray numbering) C11/C11A and C15/C15A at 0.043(1) and 0.036(1) Å above and below this plane, respectively.

A comparison of the peripheral carbon−carbon bond lengths in **1** shows that these lie within the range 1.389(2) − 1.398(2) Å (molecule A) and 1.388(2) − 1.397(2) (molecule B). In the previously reported structure,[12] the corresponding range is 1.354(8) − 1.403(8) Å. The near-planarity of the peripheral C atoms of **1** is also nicely demonstrated by their torsion angles (Table 2)

To obtain the best calculated results using ab initio methods, an infinite basis set with infinite correlation should be used. However, this ideal goal is impractical,

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Table 2. Summary of Torsion Angles for the Ring

observed torsion angles in **1**			
molecule A		molecule B	
bond (X-ray numbering)	torsion angle (deg)	bond (X-ray numbering)	torsion angle (deg)
C8−C2−C3−C4	177.4(2)	C17−C11−C12−C13	176.8(2)
C3−C2−C8−C9A[a]	−179.6(2)	C12−C11−C17−C18[b]	−179.1(2)
C2−C3−C4−C5	−3.9(2)	C11−C12−C13−C14	−4.5(3)
C3−C4−C5−C6	4.1(2)	C12−C13−C14−C15	5.0(3)
C4−C5−C6−C9	−176.7(1)	C13−C14−C15−C18	−178.7(2)
C5−C6−C9−C8[a]	179.4(2)	C14−C15−C18−C17[b]	178.7(2)

[a] $2 - x, 3 - y, 1 - z$. [b] $2 - x, 2 - y, -z$.

and in general, a compromise must be reached between the level of theory used, the size of the system under investigation, and the computational resources available. Often small basis set and semiempirical calculations are dismissed as unreliable. We propose that when using these methods, and most importantly incorporating correlation, qualitatively correct geometries will be obtained. A comparison of our AM1 CI4, our ab initio, and the DFT[1b] (all peripheral bond lengths 1.409 Å) calculated geometries for **1b** and the X-ray structure determined for **1** (Table 1) reveals excellent agreement between the sets of data. This comparison supports our contention that meaningful results can be obtained by including correlation even at the semiempirical and low-order ab initio levels.

Experimental Section

The X-ray diffraction data for **1** was collected at 173(2) K on a Siemens SMART 3-circle diffractometer (χ-axis fixed at 54.74°) equipped with a CCD detector maintained near −54 °C (Table III). The frame data were acquired with the SMART[15] software using a Siemens 3-circle platform using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). A dark green crystal of **1** was mounted on a glass capillary fixed on a copper pin and then loaded on the goniometer head. The cell constants are determined from 60 10-s frames. The unit cell parameters were different from those previously reported.[12] A complete hemisphere of data was scanned on ω (0.3°) with a run time of 30 s per frame at the detector resolution of 512×512 pixels. A total of 1271 frames were collected in three sets, and a final set of 50 frames, identical to first 50 frames, were also collected to determine crystal decay. The frames were then processed on a SGI-Indy/IndigoII workstation using the SAINT software[16] to give the *hkl* file corrected for Lp/decay. The data were corrected for absorption using the SADABS[17] program. The structures were solved by the direct method using the SHELX-90[18] program and refined by a least-squares method on F^2 using SHELXTL ver 5.03[19] with resolution set at 0.85 Å. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added at the calculated positions and refined using a riding model.[20] The crystal used for the diffraction study showed no decomposition during data collection.

Table 3. Crystallographic Data Collection/Refinement Parameters for 1

emp formula	C18 H16
formula wt	232.31
T (K)	173(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space grp	P-1
unit cell dimens	$a = 7.4202(6)$ Å, $\alpha = 78.618(2)$° $b = 7.6001(6)$ Å, $\beta = 80.9910(10)$° $c = 12.692(1)$ Å, $\gamma = 64.556(2)$°
volume, (Å^3), Z	631.53(9), 2
density (calcd) (Mg/m^3)	1.222
absorpn coeff (mm^{-1})	0.069
F(000)	248
cryst size (mm)	$0.45 \times 0.25 \times 0.10$
θ range for data collectn	1.64−28.23°
limiting indices	$-9 \le h \le 9$, $-10 \le k \le 9$, $-13 \le l \le 16$
reflns collected	4047
Indep reflns	2848 [R(int) = 0.0157]
refinemt method	full-matrix least-squares on F^2
data/restraints/param	2087/0/164
goodness-of-fit on F^2	1.054
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0389$, w$R_2 = 0.0946$
R indices (all data)	$R_1 = 0.0647$, w$R_2 = 0.1221$
extinction coeff	0.041(6)
largest diff peak and hole (e Å^{-3})	0.198 and −0.160

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Supporting Information Available: A crystal packing diagram for **1**, Table 1 (crystal data and structure refinement for **1**), Table 2 (atomic coordinates), Table 3 (bond lengths and angles for **1**), Table 4 (anisotropic displacement parameters for **1**), Table 5 (hydrogen coordinates and isotropic displacement parameters for **1**), and Cartesian coordinates for all calculated structures (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) Sheldrick, G. M. SHELXS-90, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1990.

(19) SHELXTL 5.03, Program library for Structure Solution and Molecular Graphics, Siemens Analytical Instruments Division, Madison, WI 1995.

(20) The authors have deposited atomic coordinates for **1** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.