

Table XII. MS Data for 3- and 5-Methyl-4-chloro-1,2-dihydrophosphorin 1-Oxides 4a-c

fragment ( <i>m/e</i> )	relative intensity		
	4a	4b	4c
M <sup>+</sup> <sup>a</sup>	100	84	100
[M - Cl] <sup>+</sup>	19	20	22
[M - C <sub>2</sub> H <sub>4</sub> ] <sup>+</sup>		12	3
[M - C <sub>2</sub> H <sub>5</sub> ] <sup>+</sup>		3	8
[M - C <sub>3</sub> H <sub>6</sub> ] <sup>+</sup>		65	56
[M - C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup>		31	6
[M - C <sub>4</sub> H <sub>8</sub> ] <sup>+</sup>			54
[M - C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup>			24
[M - P(O)R] <sup>+</sup> + H (115)	12	14	12
[M - P(O)R] <sup>+</sup> (114)	12	15	16
[M - P(O)R] <sup>+</sup> - H (113)	6	12	12
[C <sub>7</sub> H <sub>9</sub> ] <sup>+</sup> (91)	14	14	8
[M - (Cl + P(O)R)] <sup>+</sup> (79)	46	100	82
[C <sub>8</sub> H <sub>5</sub> ] <sup>+</sup> (77)	70	82	68
[PO] <sup>+</sup> (47)	77	34	22

<sup>a</sup> *m/e* values for the molecular ions of 4a, 4b, and 4c are 238, 204, and 218, respectively.

5- and 3-Methyl-4-chloro-3-ethoxy-1-*n*-propyl-1,2,3,6-tetrahydrophosphorin 1-Oxide 2b was prepared similarly from 1b in ethanol: yield, 49%; M<sup>+</sup><sub>found</sub> = 250.0874, C<sub>11</sub>H<sub>20</sub>ClO<sub>2</sub>P requires 250.0890; IR (neat) 2970, 1650, 1460, 1180, 1080, 750 cm<sup>-1</sup>.

Product compositions, <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR, and MS data for the mixtures containing the isomers of 2a-c are listed in Tables I, II, IV, VI, and VII, respectively.

5- and 3-Methyl-1-*n*-butyl-4-chloro-3-hydroxy-1,2,3,6-tetrahydrophosphorin 1-Oxide 3c. A solution of 1c (4.3 g, 16.9 mmol) and silver nitrate (28.7 g, 0.169 mol) in water (110 mL) was refluxed for 2 h. The mixture was filtered and extracted with two portions of chloroform (220 mL). The crude product obtained after drying over sodium sulfate and evaporating the solvent was purified by column chromatography using silica gel and chloroform-methanol (97:3) to give 3c (1.8 g, 45%) as a mixture of isomers (Table I): M<sup>+</sup><sub>found</sub> = 236.0709, C<sub>10</sub>H<sub>16</sub>ClO<sub>2</sub>P requires 236.0734; IR (neat) 3220, 2940, 1640, 1460, 1390, 1140, 750 cm<sup>-1</sup>.

5- and 3-Methyl-4-chloro-3-hydroxy-1-phenyl-1,2,3,6-tetrahydrophosphorin 1-Oxide 3a was prepared in the same way as 3c except that five times more water was used: yield, 40%; M<sup>+</sup><sub>found</sub> = 256.0471, C<sub>12</sub>H<sub>14</sub>ClO<sub>2</sub>P requires 256.0420.

5- and 3-Methyl-4-chloro-3-hydroxy-1-*n*-propyl-1,2,3,6-tetrahydrophosphorin 1-Oxide 3b was prepared similarly: yield,

42%; mp 103-111 °C; M<sup>+</sup><sub>found</sub> = 222.0554, C<sub>9</sub>H<sub>16</sub>ClO<sub>2</sub>P requires 222.0577; IR (KBr disk) 3220, 2950, 1630, 1450, 1390, 1150, 800 cm<sup>-1</sup>.

5- and 3-Methyl-4-chloro-3-hydroxy-1-methoxy-1,2,3,6-tetrahydrophosphorin 1-Oxide 3d was prepared similarly: yield, 35%; M<sup>+</sup><sub>found</sub> = 210.0241, C<sub>7</sub>H<sub>12</sub>ClO<sub>3</sub>P requires 210.0213.

Product compositions, <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR, and MS data for the isomers of 3a-d are listed in Tables I, III, V, VI, and VIII.

3- and 5-Methyl-1-*n*-butyl-4-chloro-1,2-dihydrophosphorin 1-Oxide 4c. 3c (1.2 g, 5.07 mmol) and sodium hydrogen sulfate (0.53 g, 5.07 mmol) in toluene (90 mL) was boiled for 14 h. The residue obtained after filtering and evaporating the solvent was purified by column chromatography using silica gel and chloroform-methanol (98:2) to give 4c (0.78 g, 70%) as an oily mixture of isomers: M<sup>+</sup><sub>found</sub> = 218.0654, C<sub>10</sub>H<sub>16</sub>ClOP requires 218.0629; IR (neat) 2950, 1620, 1565, 1470, 1370, 1170, 750 cm<sup>-1</sup>.

3- and 5-Methyl-4-chloro-1,2-dihydro-1-phenylphosphorin 1-Oxide 4a was prepared similarly: yield, 61%; M<sup>+</sup><sub>found</sub> = 238.0387, C<sub>12</sub>H<sub>12</sub>ClOP requires 238.0315; IR (neat) 2940, 1610, 1550, 1430, 1365, 1180, 740 cm<sup>-1</sup>.

3- and 5-Methyl-4-chloro-1,2-dihydro-1-*n*-propylphosphorin 1-Oxide 4b was prepared similarly: yield, 66%; M<sup>+</sup><sub>found</sub> = 204.0451, C<sub>9</sub>H<sub>14</sub>ClOP requires 204.0472; IR (neat) 2955, 1620, 1560, 1460, 1370, 1180, 730 cm<sup>-1</sup>.

Product compositions and <sup>31</sup>P NMR chemical shifts can be found in Table IX and <sup>1</sup>H and <sup>13</sup>C NMR and MS data in Tables X-XII.

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**Registry No.** 1a, 109011-51-0; 1b, 109011-52-1; 1c, 109011-53-2; 1d, 109011-54-3; A-*trans*-2a, 109890-86-0; A-*cis*-2a, 109890-93-9; B-*trans*-2a, 109891-00-1; B-*cis*-2a, 109891-07-8; A-*trans*-2b, 109890-87-1; A-*cis*-2b, 109890-94-0; B-*trans*-2b, 109891-01-2; B-*cis*-2b, 109891-08-9; A-*trans*-2c, 109890-88-2; A-*cis*-2c, 109890-95-1; B-*trans*-2c, 109891-02-3; B-*cis*-2c, 109891-09-0; A-*trans*-3a, 109890-89-3; A-*cis*-3a, 109890-96-2; B-*trans*-3a, 109891-03-4; B-*cis*-3a, 109891-10-3; A-*cis*-3b, 109890-97-3; A-*trans*-3b, 109890-90-6; B-*trans*-3b, 109891-04-5; A-*trans*-3c, 109890-91-7; A-*cis*-3c, 109890-98-4; B-*trans*-3c, 109891-05-6; A-*trans*-3d, 109890-92-8; A-*cis*-3d, 109890-99-5; B-*trans*-3d, 109891-06-7; B-*cis*-3d, 109891-11-4; A-4a, 109891-12-5; B-4a, 109891-15-8; A-4b, 109891-13-6; B-4b, 109891-16-9; A-4c, 109891-14-7; B-4c, 109891-17-0.

## Notes

### Crystal Structures of 4,5-Dimethyl- and 4-Methylphenanthrenes. Planarity of Congested Phenanthrene Molecules

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In view of the steric interaction in the bay region of phenanthrene, which consists of the C4, C4a, C4b, and C5 carbon atoms, there is interest in the planarity of this region in methylphenanthrenes because some of them are

carcinogenic.<sup>2</sup> However, the molecular structures of 4,5-dimethylphenanthrene (1) and 4-methylphenanthrene (2) have not been determined. The phenanthrene ring in 1 is considered to be nonplanar on the basis of observations of the racemization process for some of its derivatives<sup>3</sup> and the crystal structures of related compounds.<sup>4,5</sup> During an

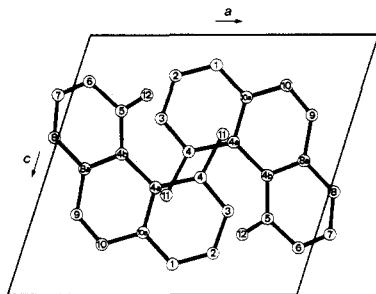
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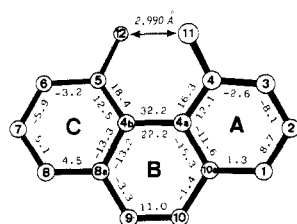
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**Figure 1.** Projection of the molecular structure of 4,5-dimethylphenanthrene (1) viewed down the *b* axis.



**Figure 2.** Selected torsional angles (deg) involving the carbon atoms in 4,5-dimethylphenanthrene (1) and the nonbonding distance between the 4- and 5-methyl carbon atoms in 1.

investigation of rotation barriers of methyl groups in crystals of methylphenanthrenes and related compounds,<sup>6</sup> we found that the two methyl groups in 1 have different chemical shifts in the <sup>13</sup>C CPMAS NMR spectra and different rotation barriers. However, we could not distinguish whether this nonequivalence originates intramolecularly or intermolecularly. We have now determined the X-ray crystallographic structure of 1 to elucidate distortion in its molecular structure and to investigate why the two methyl groups are nonequivalent.

Since molecular structures of several methylbenzophenanthrenes determined by X-ray crystallography<sup>7</sup> are more or less nonplanar, we wished to ascertain whether a planar structure in 2 could explain the observed large rotation barrier ( $5.05 \pm 0.13$  kcal mol<sup>-1</sup>)<sup>6</sup> of the 4-methyl group. Accordingly, we have attempted to obtain the crystal structure of 2 by X-ray crystallography.

### Experimental Section

**4,5-Dimethylphenanthrene.** Crystals of 1 were obtained from chloroform-ethanol. Intensity data were obtained on a Rigaku four-circle diffractometer (Mo *K* $\alpha$  radiation,  $\omega$  scanning mode, scan speed 2 deg min<sup>-1</sup>). A total of 1419 reflections ( $F > 6\sigma(F)$ ) were measured with  $2\theta < 60^\circ$ . The structures were solved by direct methods and refined by block-diagonal least-squares calculations with the X-STANP program.<sup>8</sup> The 14 hydrogen atoms in 1 were located on a D map and refinements were continued for parameter shifts to reduce their deviations to a preset limit. In the final refinement, anisotropic thermal parameters were used for non-hydrogen atoms, but isotropic temperature factors were employed for the hydrogen atoms. The final discrepancy was  $R = 0.611$  or  $R_w = 0.0648$  ( $w = 1.0$ ). The crystals are monoclinic, space group  $P2_1$ ,  $Z = 2$ ,  $a = 8.733$  (2) Å,  $b = 8.254$  (2) Å,  $c = 8.316$  (3) Å,  $\beta = 107.61$  (2)°,  $V = 571.3$  (3) Å<sup>3</sup>, and  $D_c = 1.199$  g cm<sup>-3</sup> ( $C_{16}H_{14}$ , mol wt 206.29). The projection of the structure of 1 along the *b* axis is shown in Figure 1. Bond lengths and angles involving

**Table I.** Bond Lengths and Bond Angles Involving the Carbon Atoms for 1 with Estimated Standard Deviations in Parentheses

atoms	bond lengths, Å	atoms	bond angles, deg
C1-C2	1.355 (9)	C2-C1-C10a	121.0 (5)
C1-C10a	1.400 (7)	C1-C2-C3	119.4 (4)
C2-C3	1.372 (7)	C2-C3-C4	121.9 (5)
C3-C4	1.396 (6)	C3-C4-C4a	119.0 (4)
C4-C4a	1.419 (6)	C3-C4-C11	116.6 (4)
C4-C11	1.511 (7)	C4a-C4-C11	123.9 (3)
C4a-C4b	1.472 (5)	C4-C4a-C4b	124.6 (3)
C4a-C10a	1.419 (6)	C4-C4a-C10a	117.1 (3)
C4b-C5	1.394 (6)	C4b-C4a-C10a	118.2 (4)
C4b-C8a	1.435 (6)	C4a-C4b-C5	125.2 (4)
C5-C6	1.398 (5)	C4a-C4b-C8a	116.5 (4)
C5-C12	1.511 (7)	C5-C4b-C8a	118.1 (3)
C6-C7	1.392 (8)	C4b-C5-C6	119.0 (4)
C7-C8	1.337 (9)	C4b-C5-C12	124.9 (3)
C8-C8a	1.405 (6)	C6-C5-C12	115.3 (4)
C8a-C9	1.421 (8)	C5-C6-C7	121.0 (5)
C9-C10	1.327 (7)	C6-C7-C8	120.4 (5)
C10-C10a	1.449 (8)	C7-C8-C8a	120.7 (5)
		C4b-C8a-C8	119.2 (5)
		C4b-C8a-C9	120.4 (4)
		C8-C8a-C9	120.3 (5)
		C8a-C9-C10	120.9 (5)
		C9-C10-C10a	121.6 (5)
		C1-C10a-C4a	120.1 (5)
		C1-C10a-C10	120.8 (4)
		C4a-C10a-C10	118.6 (4)

the carbon atoms of 1 are collected in Table I, and Figure 2 shows the torsional angle of its carbon atoms.

### Results and Discussion

The molecules of 1 form a column along the spiral axis passing through the center of the *ac* plane in the unit cell (Figure 1). The closest distances from the C3 carbon atom to the C4b, C8a, C8, and C5 carbon atoms of the other molecule in the unit cell are 3.486, 3.596, 3.729, and 3.777 Å, respectively, and those from the C12 carbon atom to the C3, C4, and C2 carbon atoms of the other molecule are 3.568, 3.709, and 3.762 Å, respectively. Carbon atoms belonging the different columns are separated by at least 3.82 Å. Similar molecular packing is observed for 1,12-dimethylbenz[*a*]anthracene,<sup>4</sup> in which the intermolecular distances corresponding to that between C3 and C4b and that between C12 and C3 in 1 are 3.48 and 3.55 Å, respectively, being comparable to the values in 1.

The molecular structure of 1 is notably distorted in the solid by steric repulsion between the two methyl groups in the bay region. This intramolecular strain should be relieved by in-plane deformation with lengthening of the bonds and expansion of the bond angles and also by out-of-plane distortion from the planar phenanthrene structure. All the bonds from the C4a and C4b carbon atoms are elongated, whereas the C1-C2 and C7-C8 bonds are shortened. However, the absolute changes from phenanthrene are trivial. For example, the C4a-C4b bond is only 0.015 Å longer,<sup>9</sup> and the C-C-C bond angles in the bay region are expanded by only about 2°. The torsional angles in the bay region of 1 reflect out-of-plane deformation of the molecular structure: 16.3°, 32.2°, and 18.4° for the C11-C4-C4a-C4b, C4-C4a-C4b-C5, and C4a-C4b-C5-C12 angles, respectively (Figure 2). These values are close to those of the corresponding torsional angles in 1,12-dimethylbenz[*a*]anthracene<sup>4</sup> and 4,5-dimethyl-9,10-diazaphenanthrene *N,N'*-dioxide,<sup>5</sup> and the nonbonding

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distance between the two methyl carbon atoms in 1 (2.990 Å) is 0.03 Å longer than that in the former and 0.04 Å shorter than that in the latter. Thus the in-plane deformation of the molecular structure of 1 is alleviated by the out-of-plane distortion.

MMPI molecular mechanics calculations by Kao and Allinger<sup>10</sup> indicate that the most stable geometry for an isolated molecule of 1 is nonplanar; standard deviations of the bond lengths and angles between the experimental values and those recalculated by us are 0.019 Å and 1.2°, respectively. The calculated values for the three torsional angles in the bay region are 15.7°, 40.0°, and 15.7°, which are somewhat different from the experimental values.

Now we turn to the question of the nonequivalence of the two methyl groups in 1.<sup>6</sup> The absence of noncongruent molecules in the crystalline state indicates that the two nonequivalent methyl groups should be assigned to the 4- and 5-methyl groups in 1. The intramolecular placement of the two methyl groups is similar in the crystalline state: the difference between the C11-C4-C4a-C4b and the C12-C5-C4b-C4a torsional angles is only 2.1°, and the C11 methyl carbon atom lies 0.40 Å above the average plane for ring A, while the C12 methyl carbon atom lies 0.44 Å below the average plane for ring C (Figure 2). Therefore, the nonequivalence should be ascribed to their intermolecular environment. Since the C12 methyl carbon atom is very close to the C3 carbon atom of the other molecule whereas the C11 methyl carbon atom is separated by at least 3.82 Å from any carbon atom of other molecules, these differences may account for the difference in the rotation barriers of the 4- and 5-methyl groups in the solid state. It should be noted that the C12 methyl carbon atom is only 3.525 Å above ring A of the other molecule. The difference between the <sup>13</sup>C NMR chemical shifts of the two methyl carbon atoms in 1 is mainly due to the intermolecular effect of the local anisotropy<sup>11</sup> or the so-called ring current effect<sup>12</sup>.

**4-Methylphenanthrene.** Crystals of 2 from chloroform-ethanol were subjected to X-ray analysis under the same conditions as those for 1. A total of 719 reflections were recorded with  $2\theta < 50^\circ$ , and the data were analyzed by the same procedure. However, even after the anisotropic refinements for nonhydrogen atoms in 2, we could not arrive at *R* values low enough to reveal the hydrogen peaks on the D map with any trial-disordered features included in the methyl carbon atom. Therefore, the hydrogen atoms in 2 were calculated and included in the structure-factor calculations without refining their parameters. In the final isotropic refinement, instead of isotropic thermal parameters for the hydrogen atoms, we used those for the carbon atoms to which they are attached. The final discrepancy was  $R = 0.1318$  or  $R_w = 0.1273$  ( $w = 1.0$ ).

The crystals are monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 8.661$  (3) Å,  $b = 8.976$  (2) Å,  $c = 13.716$  (4) Å,  $\beta = 98.37$  (3)°,  $V = 1055.0$  (6) Å<sup>3</sup>, and  $D_c = 1.210$  g cm<sup>-3</sup> (C<sub>15</sub>H<sub>12</sub>, mol wt 192.26). Our solution implied planar molecules stacked very closely in pairs; the distance of the C11 methyl carbon atom from the best plane through the aromatic carbon atoms of 2 is only 0.07 Å, implying a planar structure. However, because of the large *R* values, the indicated planarity of the molecule in the solid state is questionable and should be examined more carefully.

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**Registry No.** 1, 3674-69-9; 2, 832-64-4.

**Supplementary Material Available:** Tables of the final least-squares fractional coordinates for 1 and 2, the thermal parameters for 1 and 2 with stereoscopic view of the thermal ellipsoids, and the bond lengths and the bond angles involving the carbon atoms for 2 (7 pages). Ordering information is given on any current masthead page.

### Conjugate Addition Reactions of $\alpha$ -Silylated $\alpha,\beta$ -Unsaturated Carboxylic Acid Salts

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Attempts to effect conjugate addition of organometallic reagents to  $\alpha,\beta$ -unsaturated carboxylic acids are generally unsuccessful. Reactions of simple unsaturated acids with excess Grignard reagents give, in some cases, low yields of 1,4-adducts.<sup>1a-c</sup> Organolithium reagents generally give 1,2-addition products<sup>1b,2</sup> though exceptions have been noted.<sup>3</sup> Recently, successful additions to unsaturated carboxylic acids using modified organocopper reagents (RCu·BF<sub>3</sub>) have been reported,<sup>4</sup> but this method appears useful only for monosubstituted acrylic acids.

Our interest in the conjugate addition reactions of  $\alpha,\beta$ -unsaturated carbonyl systems in which 1,2-addition reactions are suppressed by the placement of a unit of negative charge adjacent to the carbonyl group (charge-directed conjugate addition reactions<sup>5</sup>) led us to examine conjugate addition reactions of strong nucleophiles with salts of acrylic acid. While low yields of 1,4-adducts with *n*-BuLi were observed, polymerization reactions dominated.<sup>6</sup> Boeckman<sup>7</sup> and Stork<sup>8</sup> previously demonstrated that the use of  $\alpha$ -silylated  $\alpha,\beta$ -unsaturated ketones in classical Michael addition reactions results in improved yields, presumably as a result of the  $\alpha$ -silyl group's aid in reducing polymerization reactions as well as its positive electronic effect on the 1,4-addition process. While silylated ketone acceptors have received the most attention, an efficient

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