

# Fulvalene Structure and Dipolar Character. The X-Ray Crystal Structures of 1-Benzyl-2-cyclopentadienylidene-1,2-dihydropyridine, 1-(2',6'-Dichlorobenzyl)-4-cyclopentadienylidene-1,4-dihydropyridine, and 2-(2',6'-Dichlorobenzyl)-1-cyclopentadienylidene-1,2-dihydroisoquinoline. Relationships between Five- and Six-Ring Bond Lengths, Five-Ring Vicinal Proton Coupling Constants, and Charge Densities

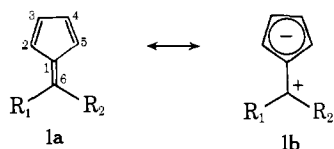
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**Abstract:** The crystal structures of the title compounds have been determined by X-ray diffractometry with Mo  $K\alpha$  radiation. The structures were solved by direct methods and refined with full-matrix least-squares techniques with anisotropic temperature factors for C, N, and Cl and isotropic terms for H. Crystal data: 1-benzyl-2-cyclopentadienylidene-1,2-dihydropyridine (**2a**), monoclinic system,  $A2/a$ ,  $a = 16.199$ ,  $b = 7.974$ ,  $c = 27.349$  Å,  $\beta = 132.02^\circ$ ,  $Z = 8$ ,  $R = 0.050$ ; 1-(2',6'-dichlorobenzyl)-4-cyclopentadienylidene-1,4-dihydropyridine (**3a**), monoclinic,  $C2/c$ ,  $a = 23.410$ ,  $b = 9.015$ ,  $c = 14.849$  Å,  $\beta = 113.48^\circ$ ,  $Z = 8$ ,  $R = 0.050$ ; 2-(2',6'-dichlorobenzyl)-1-cyclopentadienylidene-1,2-dihydroisoquinoline (**4a**), monoclinic,  $P2_1/n$ ,  $a = 12.563$ ,  $b = 12.426$ ,  $c = 12.040$  Å,  $\beta = 118.90^\circ$ ,  $Z = 4$ ,  $R = 0.043$ . The five-ring to six-ring C=C twist angles are 18.6, 2.6, and 31.2°, respectively, in **2a-4a** and the interring C=C distances are 1.410, 1.388, and 1.412 Å. About 0.025 Å of the increase from a normal ethylenic value of 1.34 Å can be attributed to the C=C twist in **2a** and **4a**, and thus an increase in the C=C distances of *ca.* 0.04 Å over 1.34 Å is due to dipolar resonance contributions.  $\pi$  delocalization in the six rings of **2a** and **4a** is greater than that in the corresponding lactams, 2-pyridone and 1-isoquinolone. The five-ring bond lengths are correlated with vicinal proton coupling constants and with five-ring charge densities obtained from CNDO/2 calculations. The large dipole moment of the 4-cyclopentadienylidene fulvalene is due to a large dipole separation rather than charge magnitude.

Aromatic hydrocarbons typically have carbon-carbon distances which are between the normal values for single and double bonds. For example, the benzene carbon-carbon distance of 1.397 Å<sup>1</sup> is about half-way between the butadiene C=C and C-C lengths of 1.341 and 1.463 Å.<sup>2</sup> Although a carbon-carbon distance of 1.39-1.40 Å has long been recognized as a fundamental property of benzenoid systems, bond length criteria have rarely been used as an experimental measure of aromaticity.<sup>3,4</sup> The reasons for this are undoubtedly associated with the (relative) difficulty of obtaining experimental bond length data from microwave, neutron, X-ray, or electron diffraction measurements. Julg<sup>5</sup> has developed an aromaticity scale based on the equality of peripheral bond distances,<sup>6</sup> but most "bond length like" assessments have used calculated bond orders.

The pentafulvenes (**1a**) have certain advantages for the investigation of bond length aromaticity relationships. These pseudo-aromatics can formally achieve a Hückel 6  $\pi$  electron configuration by delocalization of the  $\pi$  electrons in the exocyclic C=C into the five ring (**1b**), and the five-



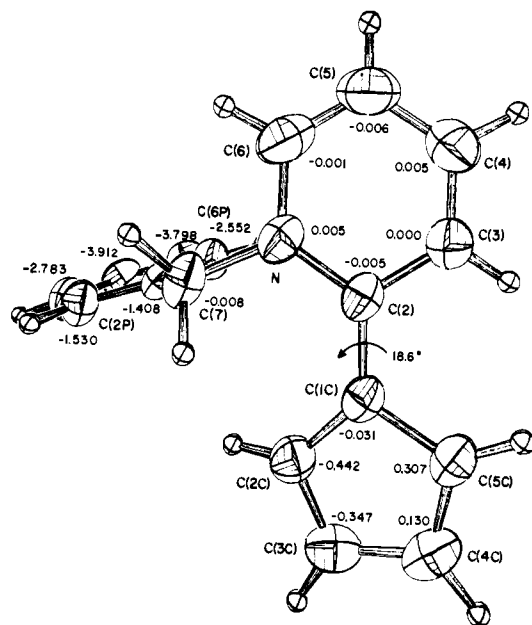
ring charge can be estimated, for example, from dipole moment data, <sup>13</sup>C NMR data, and MO calculations. In the five-ring unsubstituted pentafulvenes (i.e., C(2), C(3), C(4), and C(5) are unsubstituted), the contribution of **1b** to the ground state resonance hybrid depends on the ability of the C(6) substituent(s) (R<sub>1</sub>, R<sub>2</sub>) to stabilize the positive charge developed on C(6). For example, the dipole mo-

ments of pentafulvene (**1**, R<sub>1</sub> = R<sub>2</sub> = H) and 6-(*N,N*-dimethylamino)pentafulvene (**1**, R<sub>1</sub> = H, R<sub>2</sub> = NMe<sub>2</sub>) are 0.42<sup>7,9</sup> and 4.5 D,<sup>11</sup> respectively. Another advantage of the pentafulvenes for bond length delocalization studies is that, together with the cyclopentadienylides and cyclopentadienides, the compounds form a series with a complete spectrum of  $\pi$  electron delocalization, ranging from *ca.* 0% in pentafulvene itself to 100% in the cyclopentadienide anion.

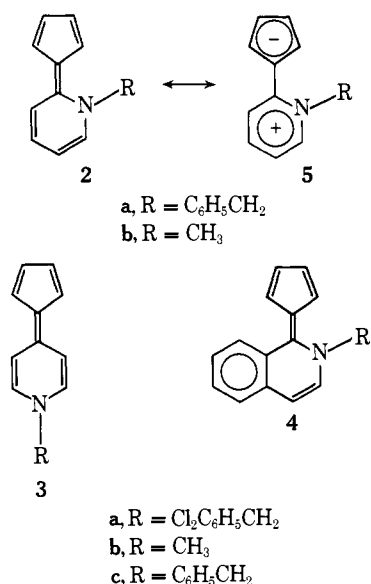
In this paper, we report the crystal structures of 1-benzyl-2-cyclopentadienylidene-1,2-dihydropyridine (**2a**), 1-(2',6'-dichlorobenzyl)-4-cyclopentadienylidene-1,4-dihydropyridine (**3a**), and 2-(2',6'-dichlorobenzyl)-1-cyclopentadienylidene-1,2-dihydroisoquinoline (**4a**). We have used these data, together with bond length and five-ring charge data from a number of other compounds, to develop relationships between five-ring charge density (e.g., **5**) and carbon-carbon lengths in the C=CC=C region of the five ring, and between the five-ring distances and NMR vicinal proton coupling constants.

## Results and Discussion

**Molecular Conformations.** ORTEP-II<sup>12</sup> drawings of **2a-4a** are shown in Figures 1-3, and bond lengths and angles are given in Figures 4-6. The individual rings in the three compounds are reasonably planar; the largest deviations from planarity occur in the 1-isoquinolinidyl moiety of **4a**. The planarity data are detailed in three tables which are included in the microfilm supplement; the data also are presented, in part, in Figures 1-3. The relatively large angles between the planes of the *N*-benzyl substituents and the planes of their respective dihydropyridine and isoquinoline rings reflect the steric factors operating between these groups, but the magnitudes of the angles, 84.4, 75.7, and 69.3° in **2a-**

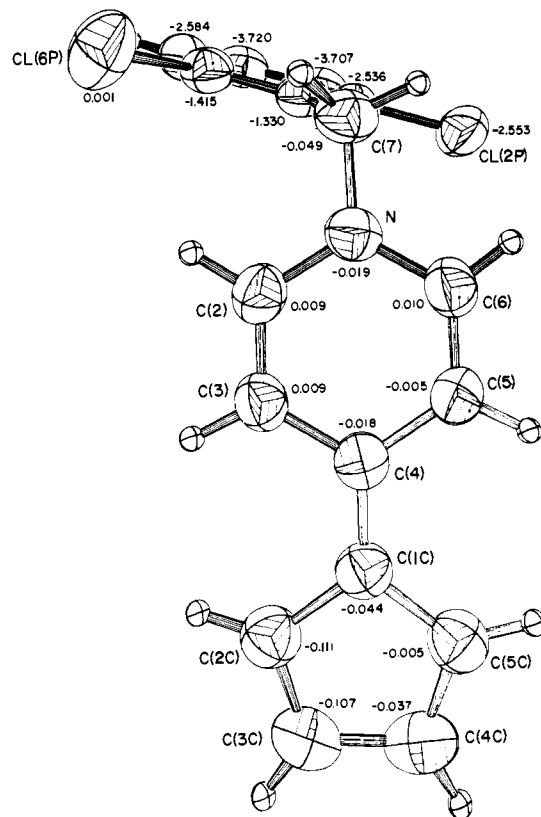


**Figure 1.** ORTEP drawing perpendicular to the dihydropyridine ring of **2a**. The numbers give the distances of the atoms from the least-squares plane of the dihydropyridine ring.

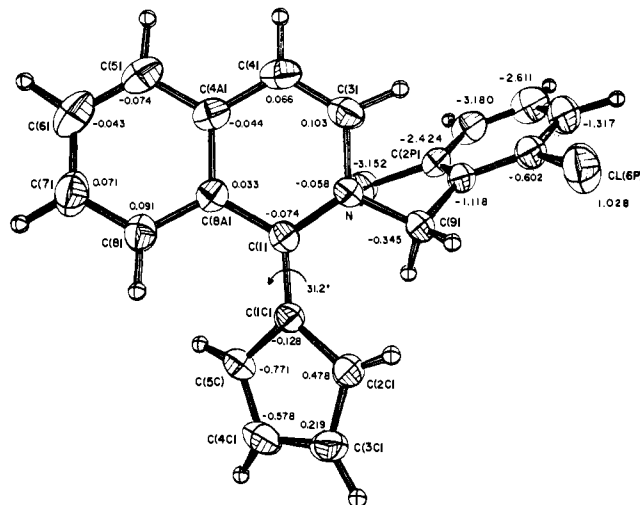


**4a**, bear no apparent relationship to the nature of the nitrogen heterocycle (pyridine or isoquinoline) or to the presence or absence of other substituents.

The angles between the normals to the five and heterocyclic six rings in the three fulvalenes have been analyzed in terms of twist and tilt components of the exocyclic C=C's connecting the rings (Table I). In the case of the 4-cyclopentadienyldenedihydropyridine (**3a**), the five- to six-ring interactions responsible for the C=C distortion are limited to relatively weak H...H contacts, and the resulting C=C twist is appropriately small at 2.6°. However, in the 2-cyclopentadienyldene derivative (**2a**), the proximity of the *N*-benzyl substituent to the double bond and to the five ring produces a substantial increase in these nonbonded interactions and the resulting twist is 18.6°. The direction of the C=C twist places the C(2C)-C(3C) side of the five ring (the side which is closest to the benzylic CH<sub>2</sub>) on the same side (below) of the dihydropyridine ring as the benzene ring. This probably means that steric interactions between the benzylic CH<sub>2</sub> and five ring are solely responsible for the



**Figure 2.** ORTEP drawing perpendicular to the dihydropyridine ring of **3a**. The numbers give the distances of the atoms from the least-squares plane of the dihydropyridine ring.



**Figure 3.** ORTEP drawing perpendicular to the dihydroisoquinoline ring of **4a**. The numbers give the distances of the atoms from the least-squares plane of the dihydroisoquinoline ring.

Table I. Exocyclic C=C Twist and Tilt Angles (deg)<sup>a</sup> in Pentafulvalenes

	Twist angle	Tilt angle <sup>b</sup>
2a	18.6	4.5
3a	2.6	0.8
4a	31.2	1.9
8	34.6	4.0

<sup>a</sup> See Experimental Section for the method of calculation. The calculations were based on the planes of the three-atom groups directly connected to the double bond termini. Calculations based on the least-squares planes of the five and six rings connected to the double bonds differed from the table values by no more than 2°.

<sup>b</sup> The angle by which the plane at one C=C end is tilted above or below the plane at the other end.

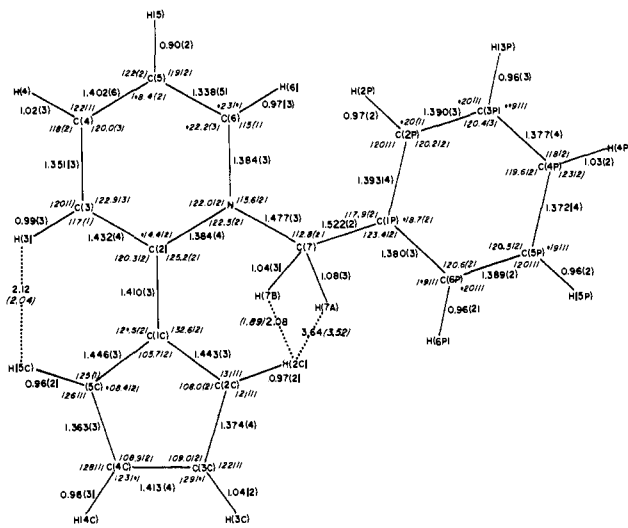


Figure 4. Bond lengths (Å), angles (deg), and esd's (in parentheses) for **2a**. The slanted H...H distances are between idealized hydrogen locations.<sup>13</sup>

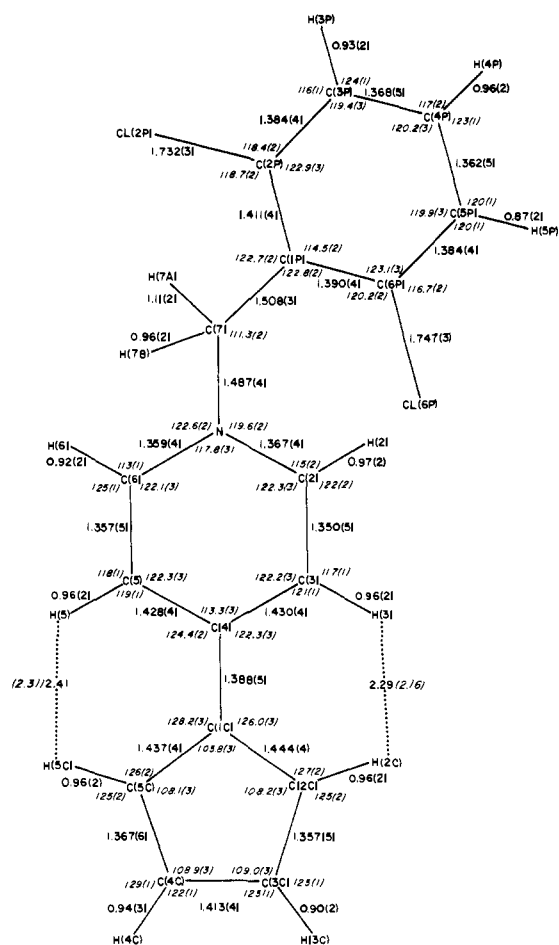


Figure 5. Bond lengths (Å), angles (deg), and esd's (in parentheses) for **3a**. The slanted H...H distances are between idealized hydrogen locations.<sup>13</sup>

C=C twist, since any steric contribution from the benzene ring should make the C=C twist in the opposite direction from that observed. The structural consequences of the benzyl...five-ring interaction can be seen in the exocyclic bond angles at N, C(2), and C(1C), in that the larger "inside" than "outside" angles permit an increase in the distances between the five ring and CH<sub>2</sub>. The most dramatic example of these angle differences is found at C(1C), where the in-

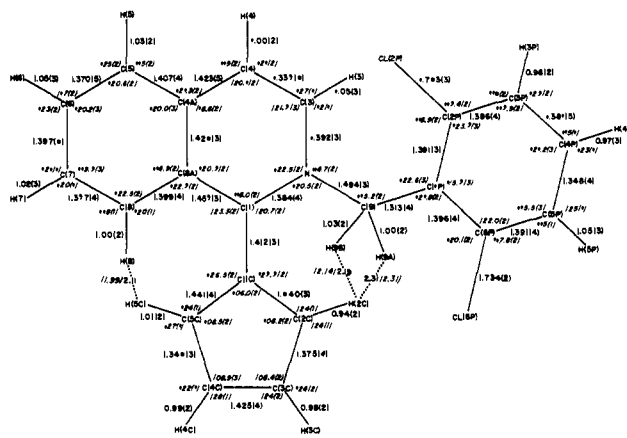


Figure 6. Bond lengths (Å), angles (deg), and esd's (in parentheses) for **4a**. The slanted H...H distances are between idealized hydrogen atom locations.<sup>13</sup>


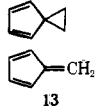
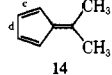
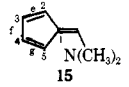
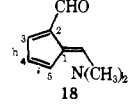
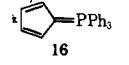
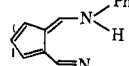
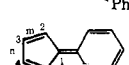
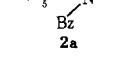
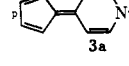
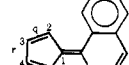
side and outside angles are 132.6 and 121.5°, respectively. Benzo annelation of the C(2)-C(3) bond in **2a** yields **4a**, and the resulting extra steric bulk on the six-ring side of the double bond in **4a** produces a twist enhancement to 31.2°. The steric pressures on both sides of the five ring must be fairly equal, since the compound shows no bond angle distortions at C(1) or C(1C).

The significant intramolecular H...H contacts are illustrated in Figures 4-6; distances between idealized hydrogen atom positions<sup>13</sup> are given as slanted numbers in parentheses. The idealized H...H contacts in the 4-cyclopentadienyldiene fulvalene (**3a**) of 2.16 and 2.31 Å<sup>14</sup> are only slightly less than the 2.4 Å van der Waals separation,<sup>15</sup> and these distances are consistent with the small 2.6° C=C twist. The shorter contacts of 1.89 and 2.04 Å in **2a**, and of 1.99 and 2.14 Å in **4a**, are not unexpected in view of the increase in C=C crowding and the resulting twists of 18.6 and 31.2°, respectively. Intermolecular forces arising from crystal packing probably are not responsible for any of the aforementioned structural features, since the majority of the intermolecular distances in the three crystal structures are longer than the appropriate van der Waals distances. The shortest intermolecular contacts are only marginally less than the H...H and H...Cl contacts of 2.4 and 3.95 Å,<sup>15,16</sup> respectively.

**Five-Ring Bond Lengths.** Bond distances in the five rings of the three fulvalenes differ substantially from the five-ring distances in simple fulvenes like pentafulvene<sup>8</sup> and 6,6-dimethylpentafulvene,<sup>17</sup> and from the C=CC=C regions in cyclopentadiene<sup>18</sup> and spiro[2.4]hepta-4,6-diene<sup>19</sup> (Table II). The C=CC=C distances in the cyclopentadienes are close to the butadiene values of 1.341 and 1.463 Å<sup>2</sup> and they are typical of localized C(sp<sup>2</sup>)=C(sp<sup>2</sup>) and C(sp<sup>2</sup>)—C(sp<sup>2</sup>) bonds,<sup>20</sup> whereas the fulvalene distances of *ca.* 1.36 and 1.42 Å reflect an appreciable degree of five-ring  $\pi$  delocalization. The effects of enhanced  $\pi$  delocalization in the fulvalenes can also be seen in the five-ring C—C bond lengths adjacent to the interring C=C; these distances are 0.02–0.04 Å shorter than normal.

**The Five-Ring to Six-Ring C=C Length.** The five-ring to six-ring double bond lengths, 1.410 Å in **2a**, 1.388 Å in **3a**, and 1.412 Å in **4a**, are long compared to normal C=C values such as the 1.34 Å length in ethylene<sup>21</sup> and the 1.347 Å C(1)—C(6) distance in 6,6-dimethylpentafulvalene,<sup>17</sup> indicating that the fulvalene connections contain appreciable amounts of single bond character.<sup>22</sup> Whereas, some of the single bond character arises from dipolar resonance forms (e.g., **5** ↔ **2**), a portion of the lengthening is due to double bond twist and perhaps to stretch produced by the five-ring

Table II. Bond Lengths (Å) and Vicinal Proton Coupling Constants (Hz) for the C=CC=C Regions of Some Five-Ring Compounds (Five-Ring Charge, e)

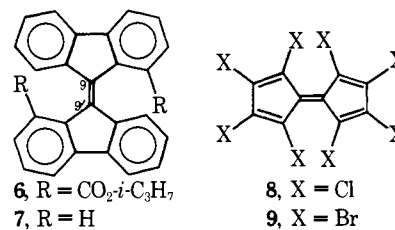
	$d(\text{C}=\text{C})$	$d(\text{CC})$	$J(\text{C}=\text{C})$	$J(\text{CC})$	$\Delta d^a$	$\Delta J^b$	$Q^c$
	1.342	1.469 <sup>d</sup>	5.06	1.94 <sup>e</sup>	0.127	3.12	
	1.341	1.460 <sup>f</sup>					
	1.355	1.476 <sup>g</sup>			0.121		0.025
	1.340	1.462 <sup>h</sup>	5.45	2.40 <sup>i</sup>	0.122	3.05	0.130
	2-3 = 1.353 4-5 = 1.362 Av = 1.358	1.414 <sup>j</sup>	2-3 = 4.55 4-5 = 4.58 Av = 4.56	2.48 <sup>k,l</sup>	0.056	2.08	0.282
	4-5 = 1.376	1.393 <sup>j</sup>	4.5	3.1 <sup>k</sup>	0.017	1.4	
	1.376, 1.393 Av = 1.384	1.401 <sup>m</sup>	3.84	2.80 <sup>i</sup>	0.017	1.04	0.840 <sup>n</sup>
	1.386, 1.389 <sup>q</sup> Av = 1.387		4.0 <sup>r</sup>				
	2-3 = 1.363 4-5 = 1.374 Av = 1.368	1.413	4.51	2.54 <sup>o</sup>	0.045	1.97	0.401 <sup>p</sup>
	1.357, 1.367 Av = 1.362	1.413	4.29	2.29	0.051	2.00	0.346 <sup>p</sup>
	2-3 = 1.375 4-5 = 1.364 Av = 1.369	1.425	4.33	2.31	0.056	2.02	0.401 <sup>p</sup>

<sup>a</sup>  $\Delta d = d(\text{CC}) - d(\text{C}=\text{C})$ . <sup>b</sup>  $\Delta J = J(\text{C}=\text{C}) - J(\text{CC})$ . <sup>c</sup> Five-ring charge (total charge on five carbons plus four hydrogen atoms) from CNDO/2 calculations. <sup>d</sup> Reference 17. <sup>e</sup> Reference 41. <sup>f</sup> Reference 18. <sup>g</sup> Reference 16. <sup>h</sup> Reference 45. <sup>i</sup> Reference 27. <sup>k</sup> A. Mannschreck and U. Kollé, *Chem. Ber.*, **102**, 243 (1969). <sup>l</sup> Crabtree and Bertelli (ref 34) reported  $J_{23} = 4.56$ ,  $J_{45} = 4.73$ ,  $J_{34} = 2.52$  Hz.  $\Delta J = 2.12$  Å is very similar to the 2.08-Hz value obtained from the data of Mannschreck and Kollé. <sup>m</sup> Reference 44. <sup>n</sup> For tri-*n*-propylphosphonium cyclopentadienylide: K. Iwata, S. Yoneda, and Z. Yoshida, *J. Am. Chem. Soc.*, **93**, 6745 (1971). <sup>o</sup> From the *N*-methyl derivative (ref 36). <sup>p</sup> From calculations on the *N*-methyl derivative. <sup>q</sup> H. L. Ammon and U. Mueller-Westerhoff, *Tetrahedron*, **30**, 1437 (1974). <sup>r</sup> U. Mueller-Westerhoff, *J. Am. Chem. Soc.*, **92**, 4849 (1970).

to six-ring steric interactions. Some previous structural work on symmetrical pentafulvalenes has pointed up several examples of long interring C=C distances which may be due to steric effects (Table III). In the case of the bisfluorenylidene **6**, the C=C length (C(9)-C(9')) = 1.39 Å and 40° twist have been cited as evidence for diradical character in the compound,<sup>23</sup> and in the octahalopentafulvalenes, **8** and **9**, the C=C lengths have been related to the loss or  $\pi$ -bond character accompanying bond twist.<sup>24,25</sup>

The difference between the 1.365 Å interring C=C distance in octachloropentafulvalene (**8**, 34.6° C=C twist) and the 1.34 Å distance in planar ethylene is 0.025 Å; similar differences exist between the five-ring to six-ring distances in **2a** (18.6° twist) and **3a** (2.6° twist), 0.022 Å, and between **4a** (31.2° twist) and **3a**, 0.024 Å. These differences suggest that 0.02–0.03 Å of the C=C lengthening in **2a**, **4a**, and **8** is due to a loss of  $\pi$ -bond character accompanying twist. Assuming that 0.02–0.03 Å of the C=C distances in twisted fulvalenes **2a** and **4a** are due to twist, and that the C=C's are not directly stretched by steric interactions,<sup>24,25b</sup> then C=C distances of 1.38–1.39 Å reflect the loss of  $\pi$ -bond character accompanying charge transfer

Table III. Interring C=C Lengths and Twist Angles in Symmetrical Pentafulvalenes

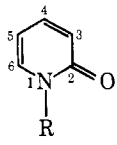
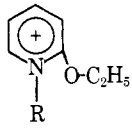
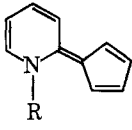
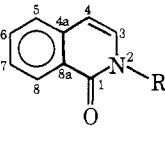
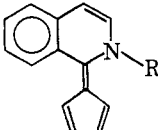


Compd	Length, Å	Twist angle, deg
<b>6</b>	1.39	40 <sup>a</sup>
<b>7</b>	1.39	43 <sup>b</sup>
<b>8</b>	1.365	36.2 <sup>c</sup>
<b>9</b>	1.385	38.5 <sup>d</sup>

<sup>a</sup> Reference 23. <sup>b</sup> N. A. Bailey, personal communication. <sup>c</sup> Reference 24. <sup>d</sup> Reference 25.

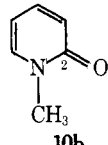
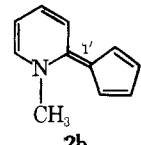
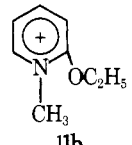
from the six to five rings<sup>26</sup> in **2a–4a**. The exocyclic C=C bonds in 6-(*N,N*-dimethylamino)pentafulvene (1.386 Å) and 2-formyl-6-(*N,N*-dimethylamino)pentafulvene (1.388 Å)<sup>27</sup> are two examples of long bonds caused by electronic

Table IV. Six-Ring Bond Lengths (Å)

					
R	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub>	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub>	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub>
Structure ref	<i>a</i>	<i>a</i>	This paper	<i>b</i>	This paper
N(1)–C(2) <sup>c</sup> or C(1)–N(2) <sup>d</sup>	1.400	1.358	1.384	1.390	1.384
C(2)–C(3) or C(1)–C(8a)	1.457	1.406	1.432	1.466	1.457
C(3)–C(4) or C(4a)–C(8a)	1.349	1.377	1.351	1.413	1.424
C(4)–C(5) or C(4)–C(4a)	1.389	1.385	1.402	1.427	1.423
C(5)–C(6) or C(3)–C(4)	1.336	1.380	1.338	1.334	1.337
N(1)–C(6) or N(2)–C(3)	1.374	1.375	1.384	1.383	1.392
C(4a)–C(5)				1.403	1.407
C(5)–C(6)				1.370	1.370
C(6)–C(7)				1.382	1.397
C(7)–C(8)				1.379	1.377
C(8)–C(8a)				1.391	1.399

<sup>a</sup> Reference 29a. <sup>b</sup> Reference 29b. <sup>c</sup> Pyridinoid numbering. <sup>d</sup> Isoquinolinoid numbering.

Table V. CNDO/2 Positive Charge Distribution in Three Pyridinoid Compounds

			
Compd	Six-ring charge, $Q_t^a$	$Q_t - Q_{C(2)}^b$	$\frac{Q_t - Q_{C(2)}}{Q_t} \times 100\%^c$
10b	0.377	0.035	10.4%
2b	0.402	0.207	51.5
11b	0.945	0.605	64.1

<sup>a</sup> Total six-ring charge including methyl group. <sup>b</sup> Total charge minus charge on C(2). <sup>c</sup> Percentage of total charge not on C(2).

reorganization and not by steric stretching. In both of these compounds, the dimethylamino groups and their respective five rings are coplanar, maximizing the dimethylamino to five-ring resonance interaction.

**Delocalization in the Six Rings.** We have performed CNDO/2 calculations on 1-methyl-2-pyridone, 2-methyl-1-isoquinolone, and 1-methyl-2-ethoxypyridinium cation, and the *N*-methyl fulvalene derivatives **2b–4b**, to obtain information on the atomic charge densities. The pyridone, isoquinolone, and pyridinium cation were included in the calculations to permit six-ring charge and delocalization comparisons with the fulvalenes. The atomic coordinates used to specify the geometries of the key molecular fragments were taken from X-ray crystallographic data, but in all cases the original N substituents of benzyl or 2,6-dichlorobenzyl were replaced by methyl.<sup>28</sup> The six-ring bond length data for the original compounds are given in Table IV; the CNDO/2 charge data for the *N*-methyl models are summarized in Tables V and VI.

Bond lengths in the six rings of the 2-pyridone (**10a**)<sup>29</sup> and the 2-cyclopentadienylidene fulvalene (**2a**) are similar, but differences of approximately 0.02 Å are found in the ring bonds at C(2), the point of ring substitution by =O in **10a** and =C<sub>5</sub>H<sub>4</sub> in **2a**. These distances are shorter in the fulvalene, reflecting an increase of double bond character in N(1)–C(2) and C(2)–C(3), and suggesting that  $\pi$  delocalization is larger in the fulvalene. However, the extent of delocalization in both of these compounds is small compared to the pyridinium cation (**11a**). We have used Julg's basic method<sup>5</sup> to calculate aromaticity indices from the peripher-

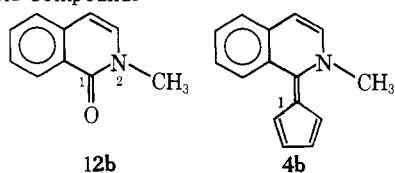
al bond lengths in the six rings in **2a**, **10a**, and **11a**. With respect to pyridine with 100% delocalization and cyclohexatriene with 0% delocalization, the percentages of delocalization are 32% in the pyridone (**10a**), 49% in the fulvalene (**2a**), and 87% in the ethoxypyridinium cation (**11a**).<sup>30</sup>

Since the overall charge separation in the fulvalene and pyridone is about the same (0.38–0.40 e; Table V), the enhanced  $\pi$  delocalization in the six ring of the fulvalene compared to the pyridone is probably related to the relative magnitudes of positive charge on C(2). The large –0.377 charge on oxygen in **10b** produces a correspondingly large positive charge (0.324) on C(2) which amounts to 90.8% of the total six-ring charge in the pyridone; hence only 9.2% of the charge is delocalized. In the fulvalene, the charge on C(1C) of the five ring is only –0.109 and the opposite charge on C(2) is 0.195; hence 51.5% of the fulvalene's six-ring charge is delocalized to other atoms. Thus we can conclude that six-ring  $\pi$  delocalization is larger in the fulvalene than in the pyridone, despite the fact that the overall magnitudes of charge separation (40–43% of the delocalization in the pyridinium cation **11b**) are approximately equal in the two systems.<sup>31</sup>

Crews, Kintner, and Padgett<sup>32</sup> have recently reported nmr coupling constants for unsaturated, six-ring, nitrogen-containing heterocycles, similar to **2**. They used the six-ring coupling constant ratio,  $J_{45}/J_{34}$ , to suggest that the amount of six-ring delocalization in **2b** was *ca.* 35% of the (complete) delocalization in pyridine. The 35% figure is in remarkably good agreement with our 40% estimate from six-ring charge densities. Interestingly, their six-ring vicinal coupling constants,  $J_{34} = 9.27$ ,  $J_{45} = 6.61$ , and  $J_{56} = 6.74$  Hz, bear little apparent relation to the corresponding carbon-carbon bond distances,  $d_{34} = 1.351$ ,  $d_{45} = 1.402$ , and  $d_{56} = 1.338$  Å, from our X-ray study of **2a**. Compared to  $J_{45}$  and  $J_{56}$ , the disproportionately large 9.27-Hz value for  $J_{34}$  may be due to steric interactions between H(3) and the five ring which could significantly increase the C(2)–C(3)–H(3) angle, reducing the H(3)···H(4) distance and altering the C(3) hybridization from the ideal  $sp^2$ .<sup>33</sup>

Although bond length differences (Table IV) between the isoquinolinoid rings in 1-isoquinolone **12a** and fulvalene **4a** are smaller than those observed in the pyridinoid system, the general patterns of positive charge distribution in **12b** and **4b** (Table VI) are virtually identical to those in **10b** and **2b**. For example, the O and C(1) charges in **12b** are –0.366 and 0.333, whereas the C(1C) and C(1) charges in **4b** are –0.112 and 0.194. Again, six-ring  $\pi$  delocalization appears

Table VI. CNDO/2 Positive Charge Distribution in Two Isoquinolinoid Compounds



Compd	Six-ring charge, $Q_t^a$	$Q_t - Q_{C(1)}^b$	$\frac{Q_t - Q_{C(1)}}{Q_t} 100^c$
12b	0.366	0.034	9.2%
4b	0.401	0.207	51.6

<sup>a</sup> Total charge on the ten isoquinolinoid atoms including the methyl group. <sup>b</sup> Total charge minus charge on C(1). <sup>c</sup> Percentage of total charge not on C(1).

to be greater in the fulvalene (**4b**) than in the lactam (**12b**), despite similar total charge separation.

**Charge Separation in the Cyclopentadienyldenedihydropyridines **2** and **3**.** Bond lengths in the five rings of **2a** and **3a** reflect the delocalization of substantial negative charge, and we have used CNDO/2 calculations on the *N*-methyl derivatives, **2b** and **3b**,<sup>35</sup> to access the relative amounts of charge separation in the compounds. The data presented in Table VII show that the large dipole moment of **3** compared to **2** is caused by a relatively large dipole separation in the compound and not by a large difference in the charge magnitudes between the fulvalenes. The distance ( $d$ ) between the positions of the positive and negative charge centers in **3** is 0.7 Å (30%) larger than in **2**, while the overall charge magnitudes ( $q$ , from  $\mu = qd$ ) are approximately equal at 0.593 e in **2** and 0.570 e in **3**. However, the total charge delocalized in the five ring of **2**, 0.401 e, is 16% greater than the corresponding quantity in **3**.<sup>36</sup>

We have also carried out CNDO/2 calculations on models of **2b** and **3b** with identical five-ring and six-ring geometries, to examine the effect of molecular geometry on charge separation. Bond lengths from the five and six rings of **2a** and **3a** were averaged to obtain a set of five- and six-ring bond lengths for the model calculations; the model five-ring geometries were identical; the six-ring geometries were slightly different to account for the position of cyclopentadienyldene substitution; C(sp<sup>2</sup>)-H and C(sp<sup>3</sup>)-H distances of 1.07 and 1.09 Å, respectively, were used throughout. The five-ring charge in the **3b** model was -0.372, the charge was -0.401 in the planar model of **2b** and -0.420 in a **2b** model with a 20° twist in the five-ring to six-ring bond.

**Five-Ring Bond Lengths, NMR Vicinal Coupling Constants and Charge.** Karplus<sup>39</sup> first showed that the magnitudes of the NMR coupling constants for vicinal protons could be correlated with a number of properties of the H-C-C-H fragment.<sup>40</sup> In the absence of variations in C-C dihedral and H-C-C angles which would effect the H...H separation, and neglecting electronic and other factors which can influence coupling constants, the vicinal proton coupling constant ( $J_{vic}$ ) should be inversely proportional to the H...H distance which, in turn, can be directly related to the C-C distance.  $J_{vic}$ , therefore, can be used to estimate C-C equality or inequality, and hence can serve as a (in)direct measure of  $\pi$ -bond delocalization in conjugated systems to the same extent that C-C distances are related to  $\pi$  delocalization. In the five-ring system, for example, the 3.5-Hz average of  $J_{C=C} = 5.06$  Hz and  $J_{C=C} = 1.94$  Hz from cyclopentadiene (Table II),<sup>41</sup> a molecule with minimal  $\pi$  delocalization, is identical to the  $J_{vic}$  from the extensively delocalized 1,2-dicarbomethoxycyclopentadienide anion.<sup>42</sup>

The majority of the previous work on  $J_{vic}$ - $\pi$  delocalization correlations has used computed  $\pi$  bond orders as the

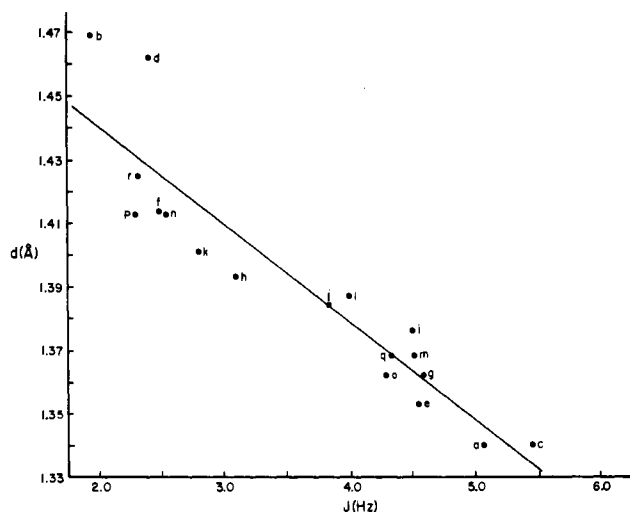


Figure 7.  $d$  (Å) vs.  $J$  (Hz) plot for eight fulvenes plus cyclopentadiene. The letters refer to specific C-C and C=C bonds in the compounds (see Table V). The equation of the line is  $d = 1.502 - 0.031J$ .

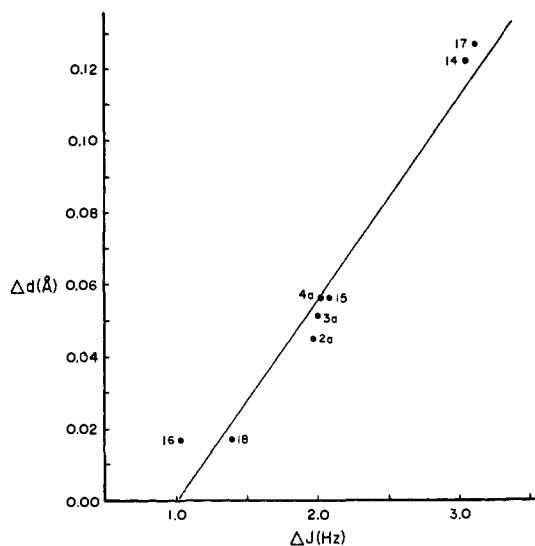
Table VII. CNDO/2 Data for the 2- and 4-Cyclopentadienyldenedihydropyridines, **2a** and **3a**

Compd	Exptl $\mu$ , D	Calcd $\mu$ , D		Dipole separation, <sup>b</sup> Å	Dipole Charge	Charge in five ring <sup>c</sup>
		Total	Charge density <sup>a</sup>			
<b>2a</b>	5.2 <sup>d</sup>	7.3 <sup>f</sup>	6.5	2.278	0.593	0.401
<b>3a</b>	8.9 <sup>e</sup>	9.3	8.1	2.973	0.570	0.346

<sup>a</sup> Evaluated from the atomic charges. <sup>b</sup> Evaluated from the average positions of the + and - atomic charges. These positions were individually computed using  $\sum r_i |q_i| / \sum |q_i|$ , where  $r_i$  is a vector from an arbitrary origin to charge  $q_i$ , which gives the location of the charge  $\sum |q_i|$  relative to the arbitrary origin. <sup>c</sup> Total charge on the five C and four H atoms. <sup>d</sup> Reference 38. <sup>e</sup> For the *N*-benzyl derivative, **3c** (ref 38). <sup>f</sup> The possibility that different amounts of C=C twist in the *N*-methyl and *N*-benzyl derivatives of **2** might have a significant dipole moment effect was investigated with a CNDO/2 calculation on a planar **2b** (i.e., C=C twist of  $\theta^\circ$ ). The total five-ring charge in the planar model was only 0.02 e less than the 18.6° twisted model; calculated  $\mu = 6.9$  D.

measure of the delocalization parameter. Studies relating  $J_{vic}$  to both bond orders and bond lengths have been reported for six rings,<sup>43</sup> whereas work on this kind of relationship for five rings has been limited to bond orders.<sup>44,45</sup> The  $J_{vic}$ -bond order correlations, which require careful and consistent parameterization of the bond order calculations, have been successful, although the more fundamental relationship is the  $J_{vic}$ -bond length one.<sup>46</sup> We have plotted the C=C-C=C bond length and vicinal coupling constant data from the five rings of cyclopentadiene, a phosphonium cyclopentadienyldene, and seven fulvenes in Figure 7 (data in Table II). A least-squares line through all 18 points has the equation  $d$  (Å) = 1.502 - 0.031 $J$  (Hz); the standard error of the population is 0.041 Å and the correlation coefficient is 0.926. Points *b* and *d*, which are for the single carbon-carbon bonds in cyclopentadiene and 6,6-dimethylpentafulvene, show the largest deviations from the line, and elimination of these data from the least-squares fit gives a 16-point equation of  $d$  (Å) = 1.475 - 0.025 $J$  (Hz); the standard error and correlation coefficient are 0.007 Å and 0.970, respectively. The  $d$ -axis intercepts (at  $J = 0$  Hz) of the two lines are without significance since it seems highly unlikely that  $J_{vic}$  would be zero for a 1.47-1.50 Å bond. That is, the  $d$  vs.  $J$  curve should terminate in the region of ca.  $d = 1.47$  Å and  $J = 2.0$  Hz.

Although the linear fits are reasonably good, some of the scatter is due to inconsistencies in the average values of



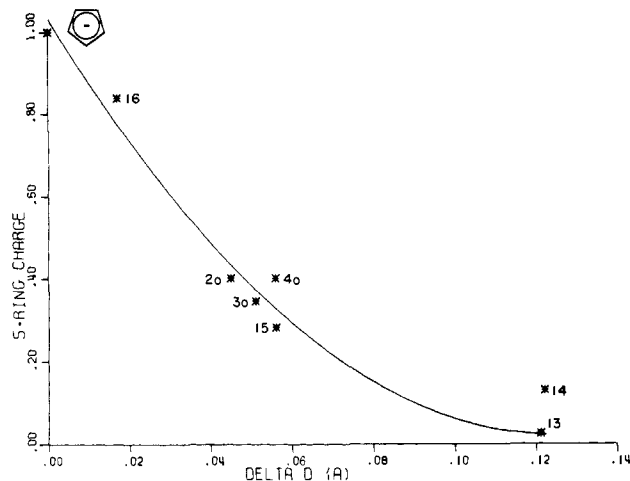
**Figure 8.**  $\Delta d$  (Å) vs.  $\Delta J$  (Hz) plot for seven fulvenes. The equation of the line is  $\Delta d = -0.059 + 0.058\Delta J$ .

$J_{C=C}$  and  $J_{C-C}$ , and of  $d_{C=C}$  and  $d_{C-C}$ , for different compounds. For example, the  $J$  averages in 6,6-dimethylpentafulvene and triphenylphosphonium cyclopentadienylide are 3.9 and 3.3 Hz, respectively, while their  $d$  averages are considerably closer at 1.40 and 1.39 Å. In an attempt to avoid the problems caused by variations in the  $J$ 's, we replotted the data for eight compounds as  $\Delta J = J_{C=C} - J_{C-C}$  vs.  $\Delta d = d_{C-C} - d_{C=C}$ . The equation of the least-squares line illustrated in Figure 8 is  $\Delta d$  (Å) =  $-0.059 + 0.058 \Delta J$  (Hz); the standard error and correlation coefficient are 0.0009 Å and 0.980, respectively.

Assuming that the  $\Delta d$  vs.  $\Delta J$  line can be linearly extrapolated to  $\Delta d = 0.0$  Å, a minimum value of 1.02 Hz is indicated for  $\Delta J$ . Although we know of no other five-ring  $\Delta d$ - $\Delta J$  data with which this minimum can be compared,  $\Delta J$  data are available for a number of highly delocalized five-ring compounds, and these data all suggest that the minimum  $\Delta J$  is close to 1 Hz. The compounds and their  $\Delta J$ 's are: triphenylarsonium cyclopentadienylide, 0.75 Hz;<sup>47</sup> dimethylsulfonium cyclopentadienylide, 0.93 Hz;<sup>47</sup> 1.1 Hz;<sup>48</sup> and trimethylammonium cyclopentadienylide, 0.88 Hz.<sup>45</sup> Although bond length data are not presently available for these compounds, calculated  $\pi$ -bond orders<sup>47</sup> suggest that  $\pi$ -delocalization should decrease from the arsonium to the sulfonium to the triphenylphosphonium cyclopentadienylide. The increase in  $\pi$ -bond order differences from the As to S to P ylides parallels the increase in  $\Delta J$ 's.

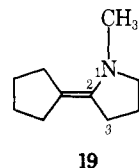
In the pentafulvenes, an increase in five-ring  $\pi$  delocalization is accompanied by an increase in the total five-ring negative charge density, e.g., localized canonical form **2**  $\leftrightarrow$  delocalized canonical form **5**. Therefore, an increase in pentafulvene  $\pi$  delocalization should cause increases in both the five-ring bond length equality and charge density.

We have correlated the total five-ring charge ( $Q$ ), evaluated from CNDO/2 calculations, with the  $\pi$ -delocalization  $\Delta d$  parameter, for six pentafulvenes plus the cyclopentadienide anion. The  $Q$  and  $\Delta d$  data are listed in Table II and plotted in Figure 9. The curve shown in Figure 9, derived by a least-squares fit with a three-term polynomial, has the equation  $Q = 1.033 - 16.237\Delta d + 65.210\Delta d^2$ . The point labeled **14** (for 6,6-dimethylpentafulvene) in the figure was omitted from the least-squares fit because inclusion of the point produced an unrealistic  $Q$  minimum in the curve at approximately  $\Delta d = 0.10$  Hz.<sup>49</sup> The root-mean-square deviation of the seven  $Q$ 's from their calculated values is 0.046.



**Figure 9.**  $Q$  (five-ring charge) vs.  $\Delta d$  plot for seven fulvenes plus cyclopentadienide. The equation of the line, which was calculated without the point for compound **14**, is  $Q = 1.033 - 16.237\Delta d + 65.210\Delta d^2$ .

**C=C Rotational Barriers.** The correspondence between the C-N distances of 1.331 Å in 6-(*N,N*-dimethylamino)pentafulvene (**15**) and 1.309 Å in 2-formyl-6-(*N,N*-dimethylamino)pentafulvene and the NMR measured  $\Delta G^\ddagger$ 's for C-N rotation of 13.5 and 17.9 kcal mol<sup>-1</sup> (**18**),<sup>50</sup> respectively, has previously been noted.<sup>27</sup> The C=C rotational barrier is the energy difference between the (planar) ground state and a dipolar, perpendicular transition state. Steric effects, which can raise the energy of the planar ground state, and electronic effects, which can stabilize charge separation in the transition state, are thought to be the main factors determining the height of the C=C barrier.<sup>50</sup> For example, the 19.1 kcal mol<sup>-1</sup>  $E_a$  for C=C rotation in 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (**19**)<sup>34</sup> is smaller than the 21.9 kcal mol<sup>-1</sup> bar-



rier<sup>34</sup> in **15**, presumably because of additional steric forces in **19** which increase the energy of the ground state by preventing the  $\text{CH}_3\text{NCCH}_2$  segment and five ring from being completely coplanar.<sup>50,51</sup> In the case of the dihydropyridinylfulvene (**2b**), the small 11.4 kcal mol<sup>-1</sup> barrier<sup>34</sup> is undoubtedly associated with better electronic stabilization of the dipolar transition state, and with an increase in the ground state energy due to steric interactions. The electronic factor is exemplified by the computed five-ring, ground-state charge densities, e.g.  $-0.28$  in **15** and  $-0.40$  in **2b**, since the same effects that enhance ground-state polarity should also stabilize the dipolar transition state. The ground-state steric effect is exemplified in **2a** by the energy raising 18.6° C=C twist and the larger "inside" angles at N, C(2), and C(1C).

### Experimental Section

Melting points are uncorrected. Ultraviolet-visible spectra were recorded on a Cary 15 spectrometer. Infrared spectra were recorded as either  $\text{CCl}_4$  or  $\text{HCCl}_3$  solutions on a Beckman IR8 spectrometer. Nuclear magnetic resonance spectra (60 MHz) were recorded on a Hitachi Perkin-Elmer R-20A spectrometer with TMS as an internal standard. Elemental analyses were performed by Dr. Franz Kasler of this Department.

**1-Benzyl-2-cyclopentadienylidene-1,2-dihydropyridine (2a)** was prepared<sup>52</sup> from 1-benzyl-2-bromopyridinium chloride and sodium

Table VIII. Crystal and Intensity Measurement Data

	1-Benzyl-2-cyclopentadienylidene-1,2-dihydropyridine	1-(2',6'-Dichlorobenzyl)-4-cyclopentadienylidene-1,4-dihydropyridine	2-(2',6'-Dichlorobenzyl)-1-cyclopentadienylidene-1,2-dihydroisoquinoline
Molecular formula	C <sub>17</sub> H <sub>15</sub> N	C <sub>17</sub> H <sub>13</sub> NCl <sub>2</sub>	C <sub>21</sub> H <sub>15</sub> NCl <sub>2</sub>
Crystallization solvent	Benzene	DMF	Chloroform
Crystal size	Red block, 0.33 × 0.44 × 0.27 mm	Purple needle, 0.25 × 0.30 × 0.40 mm	Purple plate, 0.2 × 0.3 × 0.4 mm
Space group	A2/a	C2/c	P2 <sub>1</sub> /n
Unit cell parameters (esd)	a = 16.199 (4) b = 7.974 (2) c = 27.349 (6) Å β = 132.02 (2)°	a = 23.410 (3) b = 9.0153 (5) c = 14.849 (1) Å β = 113.48 (1)°	a = 12.5631 (8) b = 12.426 (2) c = 12.040 (1) Å β = 118.90 (1)°
Average  2θ <sub>o</sub> - 2θ <sub>c</sub>  , deg	0.007	0.002	0.002
Z	8	8	4
V, Å <sup>3</sup>	2624	2874	1645
Neutral buoyancy in aq KI soln, g cm <sup>-3</sup>			
ρ <sub>exptl</sub>	1.189	1.400	1.422
ρ <sub>X-ray</sub>	1.181	1.396	1.421
R.1. vector parallel to diffractometer φ axis	[0,0,1]	[7,-1,-2]	[0,8,0]
2θ scan	2.2° at 0.5° min <sup>-1</sup>	1.4° at 1.0° min <sup>-1</sup>	2.0° at 1.0° min <sup>-1</sup>
Time per background, sec	40	20	40
Max 2θ, deg (sin θ/λ)	55 (0.6497)	55 (0.6497)	55 (0.6497)
Instability factor	8.69 × 10 <sup>-5</sup>	6.40 × 10 <sup>-5</sup>	4.46 × 10 <sup>-5</sup>
Total number of unique data (data 3σ above background)	3042 (2328)	3514 (2125)	3788 (2875)

cyclopentadienide. Recrystallization from benzene gave red, block-shaped crystals, mp 141–142° (lit.<sup>52</sup> 141–142°).

**1-(2',6'-Dichlorobenzyl)-4-cyclopentadienylidene-1,4-dihydropyridine (3a)** was synthesized<sup>53</sup> from 1-(2',6'-dichlorobenzyl)pyridinium bromide and cyclopentadiene in ethanolic sodium ethoxide. Recrystallization from DMF gave red-purple prisms, mp 199–200° (lit.<sup>53</sup> 199–200°).

**2-(2',6'-Dichlorobenzyl)-1-cyclopentadienylidene-1,2-dihydroisoquinoline (4a)** was prepared in a similar manner to Meerwein's<sup>54</sup> synthesis of 1-methyl-2-cyclopentadienylidene-1,2-dihydroisoquinoline. A solution of 3.8 g (0.01 mol) of 2-(2',6'-dichlorobenzyl)-1,1-diethoxy-1,2-dihydroisoquinoline in 20 ml of absolute EtOH was combined under N<sub>2</sub> with 2.5 ml (0.03 mol) of freshly distilled cyclopentadiene. The mixture was refluxed for 2 hr, and then cooled to 0°, precipitating the product as purple iridescent flakes. Recrystallization from DMF gave 2.6 g (74%) of purple prisms: mp 150–151°; uv (95% EtOH) λ<sub>max</sub> (ε) 2860 (5440), 3060 sh (3,300), 4730 nm (10,350); uv (10<sup>-4</sup> M acidic 95% EtOH) λ<sub>max</sub> (ε) 3480 nm (4150); NMR (CDCl<sub>3</sub>) δ 7.50 (m, 7 H, phenyl and H5–H8), 6.85 (d, 1 H, J = 7 Hz, H3), 6.60 (m, 5 H, 5 ring and H4), 5.95 (s, 2 H, CH<sub>2</sub>).

**2-(2',6'-Dichlorobenzyl)-1,1-diethoxy-1,2-dihydroisoquinoline** was prepared in a similar manner to Meerwein's<sup>54</sup> synthesis of 1-methyl-2,2-diethoxy-1,2-dihydroisoquinoline. 2-(2',6'-Dichlorobenzyl)-1-ethoxyisoquinolinium fluoroborate (2.4 g, 0.006 mol) was combined under N<sub>2</sub> with 20 ml of 0.5 M ethanolic sodium ethoxide solution, and the mixture was stirred for 4 hr at room temperature. The resulting solution, which now contained some precipitated sodium fluoroborate, was evaporated leaving a white yellow solid. The bulk of the material was extracted into dry benzene and the insoluble inorganic salt was separated by filtration. Evaporation of the solvent left a yellowish solid which was recrystallized from petroleum ether (bp 30–60°): yield 1.8 g (80%); mp 154–155°; uv (absolute EtOH) λ<sub>max</sub> (ε) 2780 sh (4790), 2850 (5260), 3030 inf (4150), 3520 nm (2,300); ir (CCl<sub>4</sub>) 1640 (s), 1290 (s), 1065 cm<sup>-1</sup> (s, broad); NMR (CDCl<sub>3</sub>) δ 7.3 (m, 7 H, phenyl and H5–H8), 6.23 (d, 1 H, J = 8 Hz, H3), 5.22 (d, 1 H, J = 8 Hz, H4), 4.90 (s, 2 H, benzyl CH<sub>2</sub>), 3.20 (2 overlapping q, 4 H, O–CH<sub>2</sub>–CH<sub>3</sub>), 1.10 (t, 6 H, J = 7 Hz, O–CH<sub>2</sub>–CH<sub>3</sub>).

Anal. Calcd for C<sub>20</sub>H<sub>21</sub>O<sub>2</sub>NCl<sub>2</sub>: C, 63.50; H, 5.59; N, 3.70. Found: C, 63.52; H, 5.67; N, 3.57.

**2-(2',6'-Dichlorobenzyl)-1-ethoxyisoquinolinium Fluoroborate.** Triethylxonium fluoroborate was prepared according to the general directions of Meerwein<sup>55</sup> from freshly distilled boron trifluoride etherate, epichlorohydrin, and dry ether (distilled from LAH). With the use of a drybox, 5.7 g (0.03 mol) of the alkylating agent was weighed and dissolved in 20 ml of dry dichloromethane (distilled from LAH). A solution of 9.1 g (0.03 mol) of 2-(2',6'-dichlorobenzyl)-1-isoquinolone in an additional 20 ml of dry dichloro-

methane was placed under N<sub>2</sub> in a three-neck flask fitted with a condenser, magnetic stirrer, and N<sub>2</sub> inlet. The solution of the alkylating agent was quickly pipeted into the reaction flask, and the mixture was stirred overnight at room temperature. Evaporation of the solvent left a yellow solid which was recrystallized from nitrobenzene-ethyl ether: yield 11.3 g (90%) of white powder; mp 150–151°; uv (absolute EtOH) λ<sub>max</sub> (ε) 2480 (7300), 2780 (9600), 2870 (9500), 3150 (3750), 3240 (4400), 3370 nm (3000); ir (CHCl<sub>3</sub>) 1070 cm<sup>-1</sup> (vs, broad, C–O–C); NMR (DMSO-*d*<sub>6</sub>) δ 8.3 (m, 1 H, isoquinoline), 7.6 (m, 6 H, isoquinoline and phenyl), 7.0 (d, 1 H, J = 7 Hz, H3), 6.6 (d, 1 H, J = 7 Hz, H4), 5.4 (s, 2 H, benzyl CH<sub>2</sub>), 4.35 (q, 2 H, J = 7 Hz, O–CH<sub>2</sub>–CH<sub>3</sub>), 1.3 (t, 3 H, J = 7 Hz, O–CH<sub>2</sub>–CH<sub>3</sub>).

Anal. Calcd for C<sub>18</sub>H<sub>16</sub>NOC<sub>2</sub>BF<sub>4</sub>: C, 51.47; H, 3.84; N, 3.33. Found: C, 51.70; H, 3.94; N, 3.18.

**2-(2',6'-Dichlorobenzyl)-1-isoquinolone.** A solution of 110 g (0.030 mol) of 2-(2',6'-dichlorobenzyl)isoquinolinium bromide in 500 ml of water was treated simultaneously with solutions of 113 g (2.0 mol) of potassium hydroxide and 210 g of potassium ferricyanide. Three recrystallizations from cyclohexane with Norite yielded 14.7 g (16%) of colorless product: mp 143–145°; uv (95% EtOH) λ<sub>max</sub> (ε) 2200 sh (30,100), 2480 (7400), 2780 (10,000), 2870 (9800), 3140 sh (4000), 3240 (4600), 3370 nm sh (3100); ir (CCl<sub>4</sub>) 1660 (vs), 1620 (s), 1430 cm<sup>-1</sup> (s); NMR (CDCl<sub>3</sub>) δ 7.6 (m, 7 H, phenyl and H5–H8), 6.90 (d, 1 H, J = 8 Hz, H3), 6.50 (d, 1 H, J = 8 Hz, H4), 5.65 (s, 2 H, CH<sub>2</sub>).

**2-(2',6'-Dichlorobenzyl)isoquinolinium Bromide.** A solution of 13 g (0.1 mol) of isoquinoline and 18 g (0.08 mol) of 2,6-dichlorobenzyl bromide in 50 ml of acetone was refluxed for 5 hr. The white salt which precipitated during reflux was filtered, washed with petroleum ether (bp 60–100°), and recrystallized twice from 95% ethanol: 22 g (75%); mp 224.5–225°; uv (95% EtOH) λ<sub>max</sub> (ε) 2340 (57,500), 2700 (4100), 2770 (4400), 3380 nm (4000); NMR (DMSO-*d*<sub>6</sub>) δ 10.15 (s, 1 H, H1), 8.3 (m, 6 H, H3–H8), 7.60 (s, 3 H, phenyl), 6.28 (s, 2 H CH<sub>2</sub>).

**General X-Ray Diffraction Experimental.** The X-ray crystallographic techniques used here have been previously detailed.<sup>56</sup> Intensity data were measured on a computer-controlled Picker FACS-I diffractometer using monochromatic Mo radiation and the 2θ–θ scan method. Crystal and intensity measurement data are listed in Table VIII.

(a) **Structure Solution by Direct Methods.** For **2a**, an *E* map computed with 279 terms (138+, 141–) revealed the 18 C and N peaks plus a single spurious peak centered in the pyridine ring. For **3a**, an *E* map computed with 502 terms (266+, 236–) revealed the 20 C, N, and Cl atoms. For **4a**, an *E* map using 915 terms (453+, 462–) revealed the 24 C, N, and Cl positions. All H atoms were located from difference maps.

(b) **Structure refinement** was done by full-matrix least-squares



Table IX. Fractional Atomic Coordinates, Thermal Parameters ( $\text{\AA}^2$ ), and Esd's (in Parentheses) for 1-Benzyl-2-cyclopentadienyldene-1,2-dihydropyridine

Atom	X	Y	Z	$U$ or $U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
N	0.4006 (1)	0.0485 (2)	0.11106 (7)	0.0378 (8)	0.052 (1)	0.049 (1)	0.0048 (8)	0.0294 (8)	0.0108 (8)
C(2)	0.3129 (1)	0.0322 (2)	0.10862 (8)	0.0339 (9)	0.049 (1)	0.037 (1)	0.0082 (9)	0.0231 (8)	0.0119 (9)
C(3)	0.2967 (2)	0.1739 (3)	0.1336 (1)	0.051 (1)	0.051 (1)	0.066 (1)	0.003 (1)	0.040 (1)	0.001 (1)
C(4)	0.3619 (2)	0.3117 (3)	0.1579 (1)	0.069 (2)	0.047 (1)	0.089 (2)	0.003 (1)	0.050 (1)	-0.001 (1)
C(5)	0.4506 (2)	0.3199 (3)	0.1600 (1)	0.070 (2)	0.051 (1)	0.100 (2)	-0.010 (1)	0.053 (2)	0.002 (1)
C(6)	0.4672 (2)	0.1899 (3)	0.1365 (1)	0.052 (1)	0.061 (2)	0.081 (2)	-0.004 (1)	0.044 (1)	0.013 (1)
C(7)	0.4308 (1)	-0.0850 (3)	0.08798 (9)	0.040 (1)	0.072 (1)	0.040 (1)	0.009 (1)	0.0286 (9)	0.010 (1)
C(1C)	0.2432 (1)	-0.1092 (2)	0.08484 (8)	0.0327 (9)	0.051 (1)	0.033 (1)	0.0025 (9)	0.0210 (8)	0.0051 (9)
C(2C)	0.5269 (2)	-0.2824 (3)	0.07620 (9)	0.041 (1)	0.053 (1)	0.043 (1)	0.002 (1)	0.0245 (9)	0.002 (1)
C(3C)	0.1651 (2)	-0.3695 (3)	0.0555 (1)	0.054 (1)	0.055 (1)	0.048 (1)	-0.007 (1)	0.027 (1)	0.000 (1)
C(4C)	0.0915 (2)	-0.2573 (3)	0.0497 (1)	0.040 (1)	0.084 (2)	0.043 (1)	-0.011 (1)	0.025 (1)	0.002 (1)
C(5C)	0.1375 (1)	-0.1010 (3)	0.06794 (9)	0.035 (1)	0.065 (1)	0.041 (1)	0.001 (1)	0.0250 (9)	0.001 (1)
C(1P)	0.5228 (1)	-0.1988 (2)	0.14341 (8)	0.0298 (9)	0.054 (1)	0.035 (1)	-0.0013 (8)	0.0217 (8)	0.0040 (9)
C(2P)	0.5671 (2)	-0.3171 (3)	0.12896 (9)	0.045 (1)	0.068 (1)	0.044 (1)	0.002 (1)	0.033 (1)	0.001 (1)
C(3P)	0.6540 (2)	-0.4200 (3)	0.1783 (1)	0.052 (1)	0.062 (1)	0.064 (1)	0.010 (1)	0.042 (1)	0.005 (1)
C(4P)	0.6970 (1)	-0.4060 (3)	0.2419 (1)	0.039 (1)	0.060 (1)	0.053 (1)	0.005 (1)	0.026 (1)	0.013 (1)
C(5P)	0.6526 (2)	-0.2912 (3)	0.25611 (9)	0.049 (1)	0.065 (1)	0.034 (1)	-0.004 (1)	0.022 (1)	0.006 (1)
C(6P)	0.5653 (1)	-0.1886 (3)	0.20704 (9)	0.045 (1)	0.058 (1)	0.038 (1)	0.003 (1)	0.0271 (9)	0.002 (1)
H(3)	0.235 (1)	0.167 (2)	0.1325 (8)	0.063 (5)					
H(4)	0.347 (2)	0.406 (3)	0.176 (1)	0.095 (7)					
H(5)	0.491 (2)	0.414 (3)	0.171 (1)	0.116 (8)					
H(6)	0.528 (1)	0.186 (2)	0.1371 (9)	0.073 (6)					
H(7A)	0.458 (1)	-0.026 (2)	0.0654 (9)	0.073 (6)					
H(7B)	0.359 (1)	-0.152 (2)	0.0514 (8)	0.058 (5)					
H(2C)	0.318 (1)	-0.340 (2)	0.0847 (8)	0.058 (5)					
H(3C)	0.155 (1)	-0.497 (3)	0.0442 (9)	0.076 (6)					
H(4C)	0.020 (2)	-0.292 (3)	0.036 (1)	0.095 (7)					
H(5C)	0.102 (1)	0.001 (2)	0.0643 (8)	0.064 (6)					
H(2P)	0.538 (1)	-0.328 (2)	0.0844 (9)	0.070 (6)					
H(3P)	0.682 (1)	-0.506 (2)	0.1680 (9)	0.074 (6)					
H(4P)	0.762 (2)	-0.484 (2)	0.2769 (9)	0.075 (6)					
H(5P)	0.680 (1)	-0.286 (2)	0.2997 (9)	0.068 (6)					
H(6P)	0.535 (1)	-0.108 (2)	0.2171 (8)	0.061 (5)					

Table X. Fractional Atomic Coordinates, Thermal Parameters ( $\text{\AA}^2$ ), and Esd's (in parentheses) for 1-(2',6'-Dichlorobenzyl)-4-cyclopentadienyldene-1,4-dihydropyridine

	X	Y	Z	$U$ or $U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(2)	1.1647 (1)	0.2955 (3)	0.4018 (2)	0.048 (2)	0.057 (2)	0.061 (2)	-0.006 (2)	0.016 (2)	-0.004 (2)
C(3)	1.2031 (1)	0.2901 (3)	0.3540 (2)	0.052 (2)	0.054 (2)	0.052 (2)	-0.001 (2)	0.016 (2)	-0.010 (1)
C(4)	1.2522 (1)	0.3950 (3)	0.3720 (2)	0.043 (2)	0.048 (2)	0.046 (2)	0.008 (1)	0.010 (1)	0.004 (1)
C(5)	1.2575 (1)	0.4997 (3)	0.4470 (2)	0.047 (2)	0.057 (2)	0.061 (2)	-0.006 (1)	0.018 (2)	-0.008 (2)
C(6)	1.2177 (1)	0.5005 (3)	0.4931 (2)	0.054 (2)	0.061 (2)	0.054 (2)	-0.002 (2)	0.016 (2)	-0.012 (2)
C(7)	1.1254 (1)	0.4036 (3)	0.5188 (2)	0.051 (2)	0.076 (2)	0.046 (2)	0.003 (2)	0.002 (1)	0.004 (2)
C(1C)	1.2910 (1)	0.3915 (3)	0.3216 (2)	0.045 (2)	0.052 (2)	0.052 (2)	0.006 (1)	0.016 (1)	0.004 (1)
C(2C)	1.2861 (1)	0.2903 (3)	0.2434 (2)	0.054 (2)	0.066 (2)	0.056 (2)	0.004 (2)	0.020 (2)	-0.003 (2)
C(3C)	1.3327 (1)	0.3214 (4)	0.2138 (2)	0.068 (2)	0.072 (2)	0.063 (2)	0.020 (2)	0.030 (2)	0.003 (2)
C(4C)	1.3685 (1)	0.4403 (3)	0.2705 (3)	0.060 (2)	0.067 (2)	0.094 (3)	0.013 (2)	0.042 (2)	0.021 (2)
C(5C)	1.3438 (1)	0.4844 (3)	0.3355 (2)	0.060 (2)	0.054 (2)	0.073 (2)	0.003 (2)	0.027 (2)	0.000 (2)
C(1P)	1.0602 (1)	0.4376 (3)	0.4461 (2)	0.049 (2)	0.059 (2)	0.041 (2)	0.001 (2)	0.022 (1)	0.004 (1)
C(2P)	1.0395 (1)	0.5833 (3)	0.4154 (2)	0.062 (2)	0.053 (2)	0.054 (2)	-0.004 (2)	0.036 (2)	-0.004 (1)
C(3P)	0.9794 (1)	0.6153 (3)	0.3502 (2)	0.071 (2)	0.064 (2)	0.057 (2)	0.022 (2)	0.035 (2)	0.017 (2)
C(4P)	0.9378 (1)	0.5020 (4)	0.3121 (2)	0.057 (2)	0.088 (2)	0.046 (2)	0.011 (2)	0.019 (2)	0.006 (2)
C(5P)	0.9553 (1)	0.3591 (4)	0.3390 (2)	0.052 (2)	0.077 (2)	0.054 (2)	-0.003 (2)	0.018 (2)	-0.003 (2)
C(6P)	1.0154 (1)	0.3285 (3)	0.4050 (2)	0.062 (2)	0.055 (2)	0.055 (2)	0.004 (2)	0.030 (2)	0.007 (1)
N	1.1701 (1)	0.4018 (3)	0.4704 (2)	0.047 (1)	0.063 (2)	0.044 (1)	0.002 (1)	0.015 (1)	-0.002 (1)
Cl(2P)	1.09125 (4)	0.72878 (9)	0.46185 (6)	0.0872 (6)	0.0646 (5)	0.1138 (7)	-0.0137 (5)	0.0602 (6)	-0.0140 (5)
Cl(6P)	1.03300 (4)	0.14282 (9)	0.43787 (9)	0.0830 (6)	0.0593 (5)	0.1195 (8)	0.0000 (5)	0.0389 (6)	0.0198 (5)
H(2)	1.131 (1)	0.223 (3)	0.390 (2)	0.077 (8)					
H(3)	1.1964 (9)	0.212 (2)	0.307 (1)	0.046 (6)					
H(5)	1.2923 (9)	0.566 (2)	0.470 (1)	0.058 (7)					
H(6)	1.2202 (9)	0.564 (2)	0.543 (1)	0.057 (7)					
H(7A)	1.130 (1)	0.299 (3)	0.560 (1)	0.070 (7)					
H(7B)	1.139 (1)	0.472 (3)	0.573 (1)	0.065 (7)					
H(2C)	1.2550 (9)	0.216 (2)	0.215 (1)	0.058 (7)					
H(3C)	1.3411 (9)	0.270 (2)	0.168 (1)	0.052 (6)					
H(4C)	1.402 (1)	0.480 (3)	0.259 (2)	0.072 (8)					
H(5C)	1.3603 (9)	0.561 (2)	0.384 (1)	0.060 (7)					
H(3P)	0.971 (1)	0.714 (2)	0.333 (2)	0.079 (8)					
H(4P)	0.897 (1)	0.529 (3)	0.264 (2)	0.089 (9)					
H(5P)	0.928 (1)	0.288 (3)	0.318 (2)	0.074 (8)					

Table XI. Fractional Atomic Coordinates, Thermal Parameters ( $\text{\AA}^2$ ), and Esd's (in Parentheses) for 2-(2',6'-Dichlorobenzyl)-1-cyclopentadienylidene-1,2-dihydroisoquinoline

Atom	X	Y	Z	$U$ or $U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	0.2245 (2)	0.4225 (2)	0.1468 (2)	0.033 (1)	0.032 (1)	0.030 (1)	0.002 (1)	0.016 (1)	0.003 (1)
C(3)	0.2134 (2)	0.5153 (2)	0.3190 (2)	0.059 (2)	0.037 (1)	0.039 (1)	-0.003 (1)	0.030 (1)	-0.004 (1)
C(4)	0.3244 (2)	0.5580 (2)	0.3644 (2)	0.061 (2)	0.033 (1)	0.037 (1)	-0.007 (1)	0.020 (1)	-0.006 (1)
C(4A)	0.3951 (2)	0.5363 (2)	0.3037 (2)	0.042 (1)	0.033 (1)	0.031 (1)	-0.001 (1)	0.012 (1)	0.003 (1)
C(5)	0.5118 (2)	0.5809 (2)	0.3487 (2)	0.044 (2)	0.046 (2)	0.045 (2)	-0.009 (1)	0.009 (1)	-0.002 (1)
C(6)	0.5736 (2)	0.5682 (2)	0.2820 (3)	0.039 (2)	0.062 (2)	0.069 (2)	-0.014 (1)	0.013 (1)	0.002 (2)
C(7)	0.5193 (2)	0.5143 (2)	0.1657 (2)	0.041 (1)	0.071 (2)	0.060 (2)	-0.010 (1)	0.026 (1)	0.003 (2)
C(8)	0.4055 (2)	0.4698 (2)	0.1214 (2)	0.035 (1)	0.055 (2)	0.043 (1)	-0.005 (1)	0.020 (1)	-0.002 (1)
C(8A)	0.3423 (2)	0.4739 (2)	0.1903 (2)	0.032 (1)	0.033 (1)	0.030 (1)	0.001 (1)	0.012 (1)	0.005 (1)
C(9)	0.0586 (2)	0.3802 (2)	0.1971 (2)	0.039 (1)	0.055 (2)	0.034 (1)	-0.007 (1)	0.023 (1)	-0.005 (1)
C(1C)	0.1693 (2)	0.3560 (2)	0.0383 (2)	0.036 (1)	0.038 (1)	0.026 (1)	-0.005 (1)	0.016 (1)	0.000 (1)
C(2C)	0.0416 (2)	0.3451 (2)	-0.0500 (2)	0.036 (1)	0.049 (2)	0.030 (1)	-0.008 (1)	0.017 (1)	-0.001 (1)
C(3C)	0.0287 (2)	0.2745 (2)	-0.1436 (2)	0.052 (2)	0.059 (2)	0.028 (1)	-0.018 (1)	0.018 (1)	-0.005 (1)
C(4C)	0.1463 (2)	0.2368 (2)	-0.1153 (2)	0.070 (2)	0.048 (2)	0.038 (1)	-0.006 (1)	0.034 (1)	-0.007 (1)
C(5C)	0.2312 (2)	0.2863 (2)	-0.0076 (2)	0.045 (1)	0.045 (2)	0.032 (1)	0.000 (1)	0.023 (1)	-0.001 (1)
C(1P)	0.0541 (2)	0.3575 (2)	0.3182 (2)	0.037 (1)	0.043 (1)	0.035 (1)	-0.007 (1)	0.021 (1)	-0.004 (1)
C(2P)	0.1397 (2)	0.2931 (2)	0.4144 (2)	0.038 (1)	0.044 (1)	0.046 (1)	-0.007 (1)	0.019 (1)	-0.007 (1)
C(3P)	0.1348 (2)	0.2667 (2)	0.5237 (2)	0.059 (2)	0.057 (2)	0.042 (1)	-0.012 (1)	0.020 (1)	0.006 (1)
C(4P)	0.0391 (3)	0.3067 (3)	0.5372 (3)	0.077 (2)	0.076 (2)	0.045 (2)	-0.023 (2)	0.037 (2)	0.004 (2)
C(5P)	-0.0484 (2)	0.3701 (2)	0.4456 (2)	0.057 (2)	0.072 (2)	0.055 (2)	-0.010 (2)	0.041 (1)	-0.003 (2)
C(6P)	-0.0407 (2)	0.3951 (2)	0.3371 (2)	0.042 (1)	0.049 (2)	0.040 (1)	-0.005 (1)	0.023 (1)	-0.002 (1)
N	0.1671 (2)	0.4431 (1)	0.2180 (2)	0.037 (1)	0.038 (1)	0.033 (1)	-0.0042 (9)	0.0209 (9)	-0.0062 (9)
Cl(2P)	0.26173 (6)	0.24302 (5)	0.39928 (7)	0.0464 (4)	0.0516 (4)	0.0689 (4)	0.0032 (3)	0.0228 (3)	-0.0079 (4)
Cl(6P)	-0.15199 (6)	0.47778 (6)	0.22505 (7)	0.0504 (4)	0.0799 (5)	0.0657 (4)	0.0151 (4)	0.0318 (4)	0.0075 (4)
H(3)	0.151 (2)	0.530 (2)	0.352 (2)	0.045 (6)					
H(4)	0.358 (2)	0.606 (2)	0.441 (2)	0.064 (7)					
H(5)	0.544 (2)	0.622 (2)	0.433 (2)	0.063 (7)					
H(6)	0.660 (2)	0.604 (2)	0.321 (2)	0.10 (1)					
H(7)	0.564 (2)	0.507 (2)	0.114 (2)	0.060 (7)					
H(8)	0.368 (2)	0.435 (2)	0.036 (2)	0.047 (6)					
H(9A)	0.059 (2)	0.312 (2)	0.154 (2)	0.053 (6)					
H(9B)	-0.018 (2)	0.421 (2)	0.133 (2)	0.045 (6)					
H(2C)	-0.019 (2)	0.386 (1)	-0.046 (2)	0.032 (5)					
H(3C)	-0.047 (2)	0.252 (2)	-0.219 (2)	0.061 (7)					
H(4C)	0.167 (2)	0.178 (2)	-0.156 (2)	0.061 (7)					
H(5C)	0.322 (2)	0.272 (1)	0.039 (2)	0.044 (6)					
H(3P)	0.201 (2)	0.224 (2)	0.589 (2)	0.067 (7)					
H(4P)	0.036 (2)	0.283 (2)	0.612 (2)	0.070 (7)					
H(5P)	-0.125 (2)	0.401 (2)	0.448 (2)	0.066 (7)					

minimizing the function  $\sum w(F_o - F_c)^2$ , where  $w = (1/\sigma(F))^2$ . Anisotropic temperature factors were employed for the C, N, and Cl atoms, and are reported here in the form  $T = \exp[-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{23}klb^*c^*)]$ ; isotropic terms were used for the H atoms. The  $F_c$ 's were corrected for isotropic secondary extinction ( $r^*$ ).<sup>57</sup> The data which were less than  $3\sigma(I_o)$  above background were included in the calculations only if  $I_c > 3\sigma(I_o)$ . The atomic coordinates are reported in Tables IX-XI.

The final agreement factors ( $R = \sum |F_o - F_c| / \sum F_o$  and wtd  $R = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$ ) are 0.050 and 0.048 for **2a**, 0.050 and 0.036 for **3a**, and 0.043 and 0.035 for **4a**.

(c) **f Curves.** Scattering factors for C, N, and Cl were generated from the analytical expressions of Cromer and Mann,<sup>58</sup> the Stewart, Davidson, and Simpson<sup>59</sup> data were used for H.

(d) **Computer Programs.** PDP-8I: P. G. Lenhart's<sup>60</sup> disk control system for the Picker FACS-I diffractometer, UNIVAC 1108: crystallographic programs,<sup>61</sup> ORTEP-II<sup>12</sup> for crystal structure illustrations; CNINDO (QCPE No. 141) for the CNDO/2 calculations;<sup>62</sup> LAOCN3 for NMR calculations.<sup>63</sup>

**NMR Spectra (100 MHz).** The  $A_2B_2$  multiplets in 1-(2',6'-dichlorobenzyl)-4-cyclopentadienylidene-1,4-dihydropyridine (**3a**) and 2-(2',6'-dichlorobenzyl)-1-cyclopentadienylidene-1,2-dihydroisoquinoline (**4a**) were recorded at 30° on a Varian HA-100 spectrometer using a 100-cycle sweep, 250-sec sweep time, and  $5 \times 1000$  spectrum amplitude, and with TMS as an internal standard. **3a** was run in saturated DMSO- $d_6$ , whereas **4a** was run in saturated  $CDCl_3$ . The five-ring multiplet in **4a** overlapped the isoquinoline ring H(3) doublet, but fortunately only the lower field half of the symmetrical  $A_2B_2$  pattern was affected.

The coupling constants and chemical shifts of the five-ring protons were obtained by least-squares techniques using the program LAOCN3. Initial values for the coupling constants were taken from the published data<sup>34</sup> for 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (**2b**). The maximum and average differences be-

tween the experimental and calculated line frequencies were 0.28 and 0.08 Hz for **3a** and 0.28 and 0.10 Hz for **4a**.

**Calculation of Double Bond Twist and Tilt.** The C=C twist ( $\alpha$ ) and tilt ( $\beta$ ) angles were obtained taking, for example, the six-ring normal as a reference vector, and determining the rotation angles ( $\alpha$  and  $\beta$ ) required to make the vector parallel to the five-ring normal. Let  $V_1$  be the six-ring normal and  $S$  a vector from the six ring to the five ring (parallel to the C=C). Then calculate  $V_2 = S \times V_1$ , normalize  $V_2$ , and calculate  $V_3 = V_1 \times V_2$ . Thus  $V_3$  is approximately parallel to  $S$ , and  $V_2$  is approximately perpendicular to  $S$  and coplanar with the six ring. The relationship between the five-ring normal ( $F$ ) and six-ring normal is

$$\begin{pmatrix} F_a \\ F_b \\ F_c \end{pmatrix} = \begin{pmatrix} \cos \beta & 0 & -\sin \beta \\ 0 & 1 & 0 \\ \sin \beta & 0 & \cos \beta \end{pmatrix} \times \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} V_{1a} \\ V_{1b} \\ V_{1c} \end{pmatrix}$$

The C=C twist angle ( $\alpha$ ) represents a right-handed rotation about  $V_3$ , and the tilt angle ( $\beta$ ) represents a right-handed rotation about  $V_2$ . If  $F$  is transformed to the  $V$  system ( $T_a = F \cdot V_1$ ,  $T_b = F \cdot V_2$ ,  $T_c = F \cdot V_3$ ) then  $\alpha = \sin^{-1} T_b$ ,  $\beta = \cos^{-1} (T_a / \cos \alpha)$  and  $\beta = \sin^{-1} (T_c / \cos \alpha)$ .

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**Supplementary Material Available.** A listing of structure factor

amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-2326.

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