detection at 205 nm. The pH of the collected fraction of $TPS_1$ was adjusted to ca. 13 with 1 M NaOH and the solution incubated at 37 °C for 35 min. One mL of this solution was neutralized and evaporated to dryness under a stream of nitrogen. Water (1 mL) was added and four 0.5-mL portions of methylene chloride were used to extract the aqueous layer. Greater than 99% of the radioactivity present was extracted. The organic extracts were combined and mixed with 200 μL of methanol containing 3α-(hydroxymethyl)-5α-androstane-3β,17β-diol (ca. 0.7 mg) and 3β-(hydroxymethyl)-5α-androstane-3α,17β-diol (ca. 0.4 mg). The organic solvents were removed under a stream of nitrogen and the contents of the tube redissolved in 200 μL of methanol. One portion of this solution was analyzed by HPLC, and a second portion was assayed for radioactivity. By isocratic elution (35% acetonitrile/water, 2 mL/min, refractive index detection) peaks corresponding to 3α-(hydroxymethyl)-5α-androstane-3β,17β-diol (39.5 mL) and 3β-(hydroxymethyl)-5α-androstane-3α,17β-diol (45 mL) were collected. Each sample was evaporated to dryness under a stream of nitrogen and assayed for radioactivity. The same procedure was followed for analysis of $TPS_2$. Base-line separation of the two steroids peaks was achieved in each experiment.

**Identification of the Acetylated Derivatives of $S_1$ and $S_2$.** $TPS_1$, collected as described above, was treated with 0.1 M NaOH (1 mL) at 37 °C for 1 h. The solution was neutrallized with 1 M HCl and extracted with methylene chloride (4 × 0.5 ml). (Less than 1% of the total radioactivity was left in the aqueous phase.) The methylene chloride was removed under nitrogen and the radioactive material treated with pyridine (2 mL redistilled from sodium hydroxide) and acetic anhydride (0.25 mL, redistilled from sodium acetate) at 22 °C for 24 h. The sample was diluted with a mixture of 3β-(acetoxymethyl)-17β-acetoxy-5α-androstan-3α-ol (1.76 mg) and 3α-(acetoxymethyl)-17β-acetoxy-5α-androstan-3β-ol (2.64 mg) in methylene chloride (200 μL) and diluted with 20 mL of ether. The ether solution was washed with neutral potassium phosphate buffer (0.323 M, 5 × 5 mL) and saturated NaCl (1 × 5 mL) and dried ($MgSO_4$), and the solvent was evaporated. A faint odor of pyridine in the residue was removed by drying under vacuum for an hour. The residue was redissolved in methylene chloride (200 μL) and a portion was assayed for radioactivity. Another portion was analyzed by HPLC (μPorasil column 3.8 × 30 mm)), using methylene chloride/hexane/acetonitrile (52:42:6, R.I. detection, 4 mL/min). The peaks corresponding to 3α-(acetoxymethyl)-17β-acetoxy-5α-androstan-3β-ol (33 mL) and to 3β-(acetoxymethyl)-17β-acetoxy-5α-androstan-3α-ol (42 mL) were collected, evaporated to dryness under nitrogen, and assayed for radioactivity. A similar procedure was followed for analysis of $TPS_2$. Base-line separation of the two steroid peaks was achieved in each experiment.

**Location of $^{18}O$ in $S_1$ and $S_2$.** A 3.2-mL aliquot of an aqueous solution containing 0.01 M phosphate (pH 7), 22.5 μM isomerase, and 19.3 μM [$^{18}O$]-**1β** was incubated at 22 °C overnight until all of the enzyme activity was gone. The inactivated enzyme was denatured and digested with trypsin, and samples of $TPS_1$ and $TPS_2$ were collected by HPLC. The solvent was evaporated and each sample was incubated at 37 °C for 3 h with 3 mL of 0.1 M NaOH. The organic material was extracted with ethyl acetate (3 × 1.5 mL) and the solvent evaporated in a stream of nitrogen. Pyridine (1 ml) and acetic anhydride (200 μL) were added, and the solution was let stand overnight. Aqueous phosphate buffer (2 mL, 0.33 M, pH 7) was added and the solution was extracted with methylene chloride (2 × 1 mL) and washed with water. The solvent was evaporated and the residue analyzed by mass spectrometry.

**Acknowledgment.** This work was supported by PHS Grant CA 24410, awarded by the National Cancer Institute, DHHS. The authors would like to thank Professors Donald Creighton, Dale Whalen, and Patrick Callery for helpful discussions. We also wish to thank Professor Callery for the mass spectral analyses.

**Registry No. 1β**, 2066-43-5; [$^3H$]-**1β**, 90991-88-1; $S_1$, 90991-84-7; $S_1$(AC), 90991-86-9; (3β-$^{18}O$)-$S_1$, 90991-91-6; (hydroxymethyl-$^{18}O$)-$S_1$, 90991-92-7; $S_2$, 90991-85-8; $S_2$(AC), 90991-87-0; EC 5.3.3.1, 9031-36-1; 3-oxo-5α-androstan-17β-ol-3-$^{18}O$, 90991-89-2; (3*S*)-spiro[5α-androstane-3,2′-oxirane]-17-one, 90991-90-5.

# Electronic Effects of Substituents in 6-Methyl-6-phenylfulvenes: $^{13}C$ NMR and Theoretical Studies[1]

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**Abstract:** The ability of substituents to alter the electron distribution in the fulvene π-system has been studied by using substituent-induced $^{13}C$ chemical shifts in a series of para-substituted 6-methyl-6-phenylfulvenes as an experimental probe, in conjunction with semiempirical molecular orbital calculations. Electron-releasing substituents lead to an overall shielding increase in the five-membered ring, but a downfield shift in the exocyclic carbon. This observation, and our CNDO calculations, suggests that (a) there is relatively little resonance interaction between the substituted phenyl group and the strongly twisted fulvene moiety and (b) the dominant mode of electron redistribution is π-polarization. Furthermore, it appears that DSP correlations may in some instances give misleading results by suggesting the operation of factors which are, in fact, absent (here, resonance effects).

While the understanding of substituent electronic effects on alternant π-systems is well advanced both experimentally[3a-c] and theoretically,[4] relatively less attention has been given to nonalternant systems, where the presence of odd-membered rings leads to markedly nonuniform π-electron distributions and high chemical reactivities.[5] Such basic questions as the role of incipiently aromatic rings in facilitating transfer of electronic perturbation, and even whether the carbons in a nonalternant π-system will be partitioned into subsets analogous to the conjugated/nonconjugated sets in alternant π-systems, and what the basis for the partitioning will be, remain largely unanswered.

In this paper we report the results of a study of the $^{13}C$ NMR spectra of a series of para-substituted 6-methyl-6-phenylfulvenes,[6] along with parallel semiempirical molecular orbital calculations,

(1) Nonalternant Systems. 2. Previous paper in this series: Holak, T. A.; Sadigh-Esfandiary; Carter, F. R.; Sardella, D. J. *J. Org. Chem.* **1980**, *45*, 2400-2404.

(2) (a) Taken in part from the M.S. thesis of C. M. Keane, Boston College, 1981. (b) Taken from the Scholar of the College (B.S.) thesis of P. Lemonias, Boston College, 1982.

(3) (a) Benzene: Olah, G. A.; Westerman, P. W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3419-3427. (b) Styrene: Hamer, G. K.; Peat, I. R.; Reynolds, W. F. *Can. J. Chem.* **1973**, *51*, 897-915. (c) Naphthalene: Kitching, W.; Bullpitt, M.; Gartshore, D.; Adcock, W.; Khor, T. C.; Doddrell, D.; Rae, I. D. *J. Org. Chem.* **1977**, *42*, 2411-2418.

(4) (a) Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496-1504. (b) Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1981**, *13*, 1-61.

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(6) $^{13}C$ NMR shift data for several 6-substituted and 6,6-disubstituted fulvenes have been previously reported: Hollenstein, R.; von Philipsborn, W.; Vogeli, R.; Neuenschwander, M. *Helv. Chim. Acta* **1973**, *56*, 847-860.

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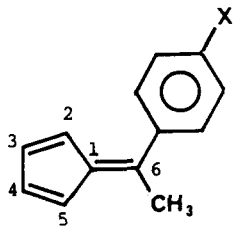
in an attempt to relate the observed substituent-induced chemical shifts to the corresponding changes in electron distribution.

## Results

The choice of 6-methyl-6-phenylfulvene (**1**) as the basic system to which perturbations would be applied was dictated by two considerations: (1) disubstitution at the exocyclic carbon would

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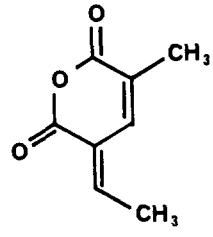


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confer sufficient stability to permit characterization and easy handling of the compounds and (2) the desire to effect the perturbations in an invariant steric environment, thus eliminating the possibility of variable sterically induced inhibition of resonance for nonaxially symmetric substituents. Interposition of a para-disubstituted phenyl ring between C-6 of fulvene and the substituent allowed this, the principal difficulty being that the twisting of the phenyl ring from coplanarity with the fulvene system made the conformation, while constant, undefined.

**Structure of 6-Methyl-6-phenylfulvene.** Inspection of Dreiding molecular models reveals that steric interaction between H-2 and the ortho hydrogens of the phenyl group makes coplanarity of the fulvene and phenyl groups impossible. To determine the degree of twist which removes the offending interactions we performed MNDO calculations[7,8] on methylphenylfulvene using molecular parameters taken from the electron-diffraction structure of 6,6-dimethylfulvene[9] and that of benzene, assuming the phenyl and fulvene fragments to be joined by a 1.471-Å single bond. Assuming both halves of the molecule to be rigid and planar, the calculated twist angle is 73°. A second calculation was performed in which the connecting bond and twist angle were allowed to vary and in which the ortho carbons of the phenyl group and C-2 of the fulvene were left free to pyramidalize. No significant deviations from planarity in either half of the molecule resulted, while the carbon–carbon bond length and the twist angle both increased slightly (to 1.48 Å and 77°, respectively). This geometry places H-2 directly above the phenyl ring, making it the most highly shielded proton in the fulvene ring (ca. $\delta$ 6.0, as opposed to $\delta$ 6.4–6.5 for the remaining three). Consistent with this assignment, von Philipsborn et al. report the fulvene protons of the 6,6-tetra-, 6,6-penta-, and 6,6-hexamethylenefulvenes to resonate between $\delta$ 6.4 and 6.5.[6]

An attempt was made to estimate the degree of nonplanarity experimentally by using the approach outlined by Webb and Yung.[10] Correlation of the $^{13}C$ shift of C-1 in the fulvene series vs. the $\beta$-carbon shift in the identically substituted styrene[3b] gave the linear relationship

$$\delta(\text{C-1}) = 0.282\delta(\text{C-}\beta) + 111.65$$

(correlation coefficient 0.982). The slope of 0.282 leads to an estimate of 58° for the twist angle, in reasonable agreement with estimates based on Dreiding models, but significantly less than those derived from the MNDO calculations. However, it is unclear to what degree the exocyclic bond in fulvene may reasonably be treated as an isolated double bond. The fact that it is strongly polarized[11] and that further polarization enhances the aromatic character of the five-membered ring may conspire to make it more susceptible to substituent-induced polarization than an isolated double bond. Thus the slope of the correlation line will be unusually large, leading to an underestimation of the twist angle.[12]

**Table I.** Proton Chemical Shifts ($\delta$) and Coupling Constants in 6-Methyl-6-(*p*-cyanophenyl)fulvene

| | H-2 | H-3 | H-4 | H-5 | Me |
|---|---|---|---|---|---|
| H-2 | 6.03 | 5.2 | 1.5 | 2.2 | 0 |
| H-3 | | 6.50 | 2.5 | 1.5 | (−) 0.6[a] |
| H-4 | | | 6.60 | 5.2 | 0 |
| H-5 | | | | 6.60 | 0 |
| Me | | | | | 2.53 |

[a] See the text for a discussion of this sign.

**Proton Spectrum of 6-Methyl-6-(*p*-cyanophenyl)fulvene.** As an aid in assigning the carbon spectra of the methylphenylfulvenes, the 79.5-MHz proton NMR spectrum of the *p*-cyano derivative was analyzed by computer simulation. The choice of the cyano derivative was dictated by the fact that the aromatic proton resonances were shifted well downfield of the fulvene protons.

All four protons of the fulvene ring are magnetically nonequivalent, giving rise to an AA'BM spectrum, of which one proton resonance appears as a doublet of triplets at $\delta$ 6.03, while the remaining three protons resonate as a complex multiplet centered at $\delta$ 6.60. Computer simulation of the spectrum using coupling constants taken from the work of Smith and Shoulders[13] reproduced the spectrum reasonably well, leading to chemical shifts of $\delta$ 6.03, 6.50, 6.60, and 6.60. However, the proton resonance at $\delta$ 6.50 displayed line broadening due to a 0.6-Hz long-range coupling with the 6-methyl protons. Assuming the $\delta$ 6.03 resonance to be due to H-2, which lies in the shielding region of the cyanophenyl ring, the analysis indicates the methyl protons to be coupled stereospecifically to H-3 across six bonds, a situation analogous to that encountered by Sardella and Vogel[14] in the anhydride (**2**) in which $^6J_{H,Me} = -0.66$ Hz.[15] Similar evidence for long-range coupling in 6,6-dibenzylfulvene was reported by Smith and Shoulders, although neither the magnitude nor the stereochemistry of the coupling were determined.[13] The chemical shifts and coupling constants for the fulvene protons of 6-methyl-6-(*p*-cyanophenyl)fulvene are summarized in Table I. The spectra of the other substituted methylphenylfulvenes were not analyzed but are similar to that of the *p*-cyano derivative.

**Assignment of $^{13}C$ NMR Spectra.** The spectra of the 6-methyl-6-phenylfulvenes exhibit 10 resonances due to the four nonequivalent phenyl and six nonequivalent fulvene carbons. They were differentiated and assigned by various methods, including relative intensities, comparison of spectra of 6-phenyl- and 6-methyl-6-phenylfulvenes, $^{13}C$–$^{19}F$ coupling constants, and correlated off-resonance decoupling experiments.

Assignment of the protonated aromatic carbons was based on the fact that they were the most intense peaks in the spectrum and on additivity relationships. An independent check was possible for 6-methyl-6-(*p*-fluorophenyl)fulvene, in which the aromatic carbon resonances are split into doublets by coupling to fluorine. Thus the doublets centered at $\delta$ 162.9 ($J_{CF}$ = 248.3 Hz), 138.2 ($J_{CF}$ = 3.4 Hz), 131.0 ($J_{CF}$ = 7.1 Hz), and 114.9 ($J_{CF}$ = 21.5 Hz) correspond to the carbons directly bonded, para, meta, and ortho to fluorine, respectively. Of the remaining singlets ($\delta$ 148.2, 143.8, 132.0, 131.8, 123.5, and 121.2), the two at low field are assigned to C-6 and C-1, owing to their low intensities. The identification

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(8) Dewar, M. J. S.; Thiel, W., Quantum Chemistry Program Exchange, No. 428.

(9) Chiang, J. F.; Bauer, S. *J. Am. Chem. Soc.* **1970**, *92*, 261–265.

(10) Webb, J. G. K.; Yung, D. K. *Can. J. Chem.* **1983**, *61*, 488–493.

(11) For instance, Huckel MO calculations on fulvene gave $\pi$-electron densities for C-1 and C-6 of 1.047 and 0.622, respectively, while CNDO calculations give $\pi$-densities of 1.038 and 0.899, respectively.

(12) The opposite behavior would be expected for a bond polarized in the reverse sense, e.g., the exocyclic bond in a heptafulvene.

(13) Smith, W. B.; Shoulders, B. A. *J. Am. Chem. Soc.* **1964**, *86*, 3118.

(14) Sardella, D. J.; Vogel, G. *J. Phys. Chem.* **1970**, *74*, 4532–4537.

(15) A five-bond coupling ($^5J_{HH}$ = +1.40 Hz) of similar stereochemistry occurs in 6-*tert*-butylfulvene.[6] Since long-range couplings across $\pi$-systems generally change sign when H is replaced by methyl,[16] this observation also suggests the six-bond coupling in (*p*-cyanophenyl)methylfulvene to be negative.

(16) Barfield, M.; Chakrabarti, B. *Chem. Rev.* **1969**, *69*, 757.

**Table II.** $^{13}C$ Chemical Shifts in Para-Substituted 6-Methyl-6-phenylfulvenes

| carbon | $NH_2$ | $CH_3O$ | $CH_3$ | H | F | Cl | Br | $CH_3CO$ | CN |
|---|---|---|---|---|---|---|---|---|---|
| C-1 | 142.20 | 142.98 | 143.30 | 143.62 | 143.79 | 143.99 | 143.95 | 144.41 | 144.67 |
| C-2 | 123.74 | 123.72 | 123.79 | 123,76 | 123.46 | 123.36 | 123.34 | 123.31 | 122.92 |
| C-3[a] | 130.72 | 131.31 | 131.58 | 131.86 | 132.03 | 132.26 | 132.28 | 132.60 | 133.04 |
| C-4[a] | 130.65 | 131.16 | 131.24 | 131.47 | 131.81 | 131.99 | 132.01 | 132.25 | 132.83 |
| C-5[b] | 121.06 | 121.13 | 121.08 | 121.08 | 121.19 | 121.16 | 121.15 | 121.14 | 121.18 |
| C-6 | 150.38 | 149.54 | 149.82 | 149.56 | 148.18 | 147.79 | 147.79 | 147.65 | 146.62 |
| $CH_3$[c] | 22.63 | 22.50 | 22,56 | 22.58 | 22.61 | 22.24 | 22.39 | 22.20 | 22.24 |
| ipso | 132.19 | 134.58 | 139.32 | 142.21 | 138.2 (3.4)[d] | 140.54 | 141.02 | 146.70 | 146.45 |
| ortho | 131.19 | 130.91 | 129.32 | 129.22 | 131.0 (7.1)[d] | 130.53 | 131.15 | 127.30 | 129.75 |
| meta | 114.27 | 113.48 | 128,64 | 127,90 | 114.9 (21.5)[d] | 128.35 | 130.79 | 129.83 | 131.73 |
| para | 147.10 | 160.04 | 138,25 | 128.34 | 162.9 (248.3)[d] | 134.42 | 122.60 | 136.50 | 111.81 |
| others | | 55.33 | 21,19 | | | | | 197.20 | 118.61 |
| | | | | | | | | 26.40 | |

[a] Assignments arbitrary and could be interchanged. [b] Average chemical shift $\delta$ 121.13 ± 0.05. No significant variation. [c] Average chemical shift $\delta$ 22.47 ± 0.16. No significant variation. [d] Numbers in parentheses represent C–F coupling constants.

**Table III.** Correlation of $^{13}C$ Shifts with Hammett's $\sigma_p$[a]

| carbon | slope | intercept | corr coeff |
|---|---|---|---|
| 1 | 1.917 | 143.48 | 0.990 |
| 2 | −0.669 | 123.55 | 0.893 |
| 3[b] | 1.793 | 131.80 | 0.998 |
| 4[b] | 1.677 | 131.56 | 0.994 |
| 5[c] | | | |
| 6 | −3.106 | 148.88 | 0.954 |

[a] Values for $\sigma_p$ taken from: O. Exner In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10. [b] Assignments are arbitrary and may be reversed. [c] Not included in the analysis; no significant variation observed.

**Table IV.** DSP Analysis of $^{13}C$ Chemical Shifts in Terms of $\rho_I$ and $\rho_R^\circ$

| carbon | $\rho_I$ | $\rho_R$ | $\lambda$ | corr coeff |
|---|---|---|---|---|
| 1 | 1.824 | 2.565 | 1.41 | 0.956 |
| 2 | −1.066 | −0.685 | 0.64 | 0.981 |
| 3 | 1.987 | 2.051 | 1.03 | 0.989 |
| 4 | 1.838 | 2.356 | 1.28 | 0.976 |
| 5 | | | | |
| 6 | −4.571 | −3.141 | 0.69 | 0.988 |

of the chemical shift of C-6 as $\delta$ 148.2 is based on the expectation (based on MNDO calculations; see below) that C-6 will have a substantially lower electron density than C-1, consistent with the previous assignments of von Philipsborn et al. for 6-alkyl- and 6,6-dialkylfulvenes.[6] Once again, a check of the assignments is possible by comparison of the spectra of 6-(p-anisyl)fulvene and 6-(p-anisyl)-6-methylfulvene. Methyl substitution at C-6 causes a pronounced downfield shift of C-6 (from $\delta$ 138.4 to 149.5) and a slight upfield shift of C-1. A similar difference is observed in the spectra of 6-(*p*-dimethylamino)fulvene and 6-(*p*-aminophenyl)-6-methylfulvene ($\Delta\delta$(C-6) = 10.7) and of fulvene[6] and 6,6-dimethylfulvene.[2a]

The protonated fulvene carbons occur as a closely spaced pair in the range $\delta$ 130–132 ($\Delta\delta$ ~0.2) and a more widely spaced pair at $\delta$ 121–124 and are assigned to C-3/C-4 and C-2/C-5 respectively, on the basis of assignments of von Philipsborn.[6] While our data did not permit C-3 and C-4 to be differentiated unambiguously, correlated off-resonance decoupling experiments on the higher field pair revealed the carbon at $\delta$ 123.5 to be bound to the most-shielded fulvene proton. Since H-2 lies in the shielding region of the phenyl group (see the section on MNDO calculations), this establishes the assignments of C-2 and C-5 as $\delta$ 123.5 and 121.2, respectively.

The 6-methyl carbon resonances all fell in the range $\delta$ 22.46 ± 0.13. Final assignments of all carbons are summarized in Table II.

## Discussion

Inspection of the data in Table II reveals that the six fulvene carbons can be grouped into three sets, which differ in their responses to substitution at the para position of the 6-phenyl ring. Carbons 2 and 5 are virtually insensitive to the nature of the substituent (C-5 exhibits a shift of $\delta$ 121.13 ± 0.05, while C-2 varies by only 0.8 ppm on going from *p*-amino to *p*-cyano substituents). Of the remaining four carbons, all of which exhibit shift variations of between 2.2 and 3.8 ppm across the series, carbons 1, 3, and 4 shift upfield with increasing electron-releasing groups, while C-6 is unique both in being the most sensitive to substitution ($\Delta\delta$ = 3.76) and in shifting *downfield* with increasingly electron-releasing substituents, indicative of loss of electron density. These observations are given quantitative expression in Table III, where the results of correlations with $\sigma_p$ are summarized. Carbons 1, 3, and 4 give excellent fits and carbon 6 gives a good fit, while C-2 gives a poor correlation, making the negative slope of doubtful significance.

The observation of an inverse substituent effect at C-6 suggests the operation of a $\pi$-polarization effect[17,18] as a significant (and perhaps the dominant) mode of substituent-induced electron redistribution in the 6-methyl-6-phenylfulvenes. Our estimate that the $\pi$-system is twisted from planarity by approximately 70–80° indicates that resonance interaction between the phenyl and fulvene $\pi$-subsystems will be seriously attenuated. Thus, a para substituent on the phenyl ring will cause a $\pi$-electron excess or deficiency at the carbon para to it (the ipso carbon), and repulsion (or attraction) between this charge and the electron density at C-6 will polarize the fulvene $\pi$-system. Within the framework of PMO theory,[19] this can be accomodated by a change ($\Delta\alpha$) in the Coulomb integral of C-6. The first-order correction to the $\pi$-electron densities at the various carbons is then

$$\Delta q_j = 4\Delta\alpha_i\pi_{ij} \quad (1)$$

where $\pi_{ij}$ are the atom–atom polarizibilities. For fulvene, this leads to the prediction that electron-releasing groups will cause a loss of $\pi$-density (hence a downfield shift) at C-6 ($\pi_{66}$ = −0.558), little effect at C-2 and C-5 ($\pi_{62} = \pi_{65}$ = 0.030), and increased electron density (hence an upfield shift) at C-1, C-3, and C-4 ($\pi_{61}$ = 0.258; $\pi_{63} = \pi_{64}$ = +0.119), as we observe. It is also noteworthy that C-1 is predicted to be more sensitive to substitution than C-3 and C-4, again in agreement with observation.

The expected effect of electron release via resonance can be gauged by comparison of the $\pi$-densities of fulvene and 6-vinylfulvene.[20] Conjugative electron release is anticipated to lead to a large increase in $\pi$-density at C-6 (−0.105 $e^-$) and a much smaller and uniform increase at the other five carbons (−0.026 $e^-$ each), inconsistent with what we infer from the $^{13}C$ shift data.

In an attempt to distinguish between resonance and inductive effects in the phenylfulvenes, we performed DSP analyses[21] of the

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(20) Streitwieser, A.; Brauman, J. A. "Supplemental Tables of Molecular Orbital Calculations"; Pergamon Press: 1965.
(21) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. chem.* **1973**, *10*, 1.

Table V. π-Electron Densities (CNDO/2) in the Fulvene Portions of Some Para-Substituted 6-Phenylfulvenes

| substituent | π-density | | | | | | |
|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | Σ(1-6) |
| $NH_2$ | 1.031 | 1.043 | 1.010 | 1.013 | 1.038 | 0.903 | 6.038 |
| OH | 1.024 | 1.045 | 1.006 | 1.010 | 1.039 | 0.910 | 6.034 |
| $CH_3$ | 1.022 | 1.044 | 1.008 | 1.009 | 1.039 | 0.910 | 6.032 |
| H | 1.020 | 1.044 | 1.006 | 1.008 | 1.039 | 0.912 | 6.029 |
| Cl | 1.017 | 1.047 | 1.001 | 1.005 | 1.042 | 0.915 | 6.027 |

fulvene $^{13}C$ shift data, with results shown in Table IV. The quality of the correlations for C-1 and C-6 improved markedly, while those for C-2, C-3, and C-4 were slightly inferior to the single-parameter fits. Interestingly, despite the likelihood that the phenyl and fulvene π-systems are almost orthogonal, the analyses appeared to implicate both resonance and inductive effects of substituents as determinants of $^{13}C$ shift variations (hence, presumably, electron density redistribution) in the phenylfulvenes, as evidenced by the comparable magnitudes of the regression coefficients $\rho_I$ and $\rho_R$. Moreover, the patterns of induced charges inferred from the ρ-values for both the putative inductive and resonance components are qualitatively the same and in agreement with that expected for π-polarization, but not for electron release by resonance, raising the question of whether the parameters derived from the DSP analysis are physically meaningful. An indication that the resonance effect is not significantly operative comes from the average chemical shift of the fulvene carbons, which is virtually constant at δ 133.43 ± 0.14, across the entire series from *p*-amino to *p*-cyano methylphenylfulvenes, with a total range of 0.43 ppm (for comparison, the range on going from aniline to benzonitrile is 2.35 ppm[22]). When the figure 180 ppm/π-electron is used, this shift range corresponds to a variation of only 0.014 electron, suggesting negligible electron release into the fulvene system.

In order to address this question more directly, we performed CNDO/2 calculations[23] on a series of para-substituted 6-phenylfulvenes. As before, the geometry was synthesized from experimental data for 6,6-dimethylfulvene and the appropriate substituted benzenes, with the phenyl–fulvene carbon–carbon bond length set at 1.471 Å. Here, however, to allow for the possibility that our estimate of 70–80° for the twist angle was seriously in error, we assumed a twist angle of only 50° (the angle which sets the internuclear distance between the sterically opposed hydrogens at 2.4 Å—twice the older value for the van der Waals radius of hydrogen).[24] The relevant π-electron density data are given in Table V. Two points worthy of immediate note are, first, the virtual constancy of the total π-density within the fulvene system at 6.032 ± 0.004, and, second, the major redistribution of electron density effected by substitution in the phenyl ring, again indicating the absence of conjugative electron release and the presence of π-polarization.

To test whether the apparent operation of a resonance effect within the fulvene π-system might be an artifact of the statistical procedure, we also performed DSP analyses of the fulvene π-electron densities using $\sigma_I$ and $\sigma_R°$, with the results shown in Table IV. Here, as in the case of the $^{13}C$ chemical shifts, the analysis appears to disclose the operation of resonance interaction between substituents and fulvene, even though the absence of any increase in total π-density in the fulvene system with increasingly strong π-donor substituents eliminates this possibility. Thus, we conclude that the major cause of substituent-induced $^{13}C$ chemical shift variation (and, therefore, π-density redistribution) in the para-substituted 6-methyl-6-phenylfulvenes is π-polarization, although the differing sensitivities of C-2 and C-5 (and, to a lesser extent, of C-3 and C-4) to substitution likely signals the superimposition of some other, albeit less important, effect.

A second point emerging from this work is that application of DSP analyses may lead to erroneous conclusions, signalling the apparent operation of an effect which is, in fact, absent. A partial explanation of how this may occur in the present case is as follows. The para substituents are capable of interacting with the phenyl ring by a variety of mechanisms, at least one of which is resonance. This leads to induction of a charge at the ipso carbon (i.e., para to the substituent), whose magnitude is dependent upon $\sigma_R°$. This charge polarizes the fulvene π-system. Since the extent of polarization depends upon the size of the charge at the ipso carbon, DSP analysis of the fulvene shifts (or densities) will show a dependence upon $\sigma_R°$. It must, however, be admitted that this explanation is, at best, partial, since it seems reasonable to expect that λ-values (i.e., $\rho_R/\rho_t$) for the various fulvene carbons would then be the same, which is not the case.

Finally, while the application of DSP analysis to highly twisted systems is, in any case, tenuous at best, the appearance of an artifact like that described here may be expected even for a planar system in which conjugation between two π-subsystems is minimal, for instance in a cross-conjugated system.

## Experimental Section

**Synthesis.** The 6-methyl-6-phenylfulvenes were synthesized by the condensation of potassium cyclopentadienide with the appropriate para-substituted acetophenone, in methanol.[25] Products were purified in most cases by column chromatography. Seven of the nine compounds were viscous liquids which tenaciously retained small amounts of solvent. This, combined with their tendency to decompose on standing, prevented our obtaining accurate elemental analyses. These compounds were thus characterized by their mass spectra ($M^+$) and their $^{13}C$ and $^1H$ NMR spectra (see the Results section).

**6-Methyl-6-phenylfulvene** was prepared as described by Kice and Parham.[26]

**6-Methyl-6-(*p*-aminophenyl)fulvene.** A solution of potassium hydroxide (9.5 g) in methanol (25 mL), contained in a two-neck round-bottom flask fitted with a reflux condenser and an addition funnel, was cooled to 0–5 °C in an ice bath. To this was added dropwise, with stirring under a nitrogen atmosphere, a solution containing 0.078 mol each of *p*-aminoacetophenone and freshly prepared monomeric cyclopentadiene in methanol (12.5 mL), at a rate sufficient to keep the temperature below 10 °C. The color of the reaction mixture changed to dark red-orange. When addition was complete, the ice bath was removed and the reaction mixture was allowed to remain at room temperature for 2 h. The reaction mixture was then added to water (50 mL) and extracted several times with petroleum ether. The combined extracts were washed with water and dried ($Na_2SO_4$), and the solvent was removed in vacuo. Purification of the crude product by column chromatography (silica gel; $CH_2Cl_2$ eluant) afforded 0.33 g (2.3%) of a bright orange oil, 6-methyl-6-(*p*-aminophenyl)fulvene. MS, *m/e* 183 ($M^+$), 168 ($M - CH_3$), 167 ($M - NH_2$).

**6-Methyl-6-(*p*-anisyl)fulvene.** A mixture of *p*-methoxyacetophenone and cyclopentadiene (0.300 mol each) in methanol was added dropwise to KOH (0.6 mol) in methanol, as described above. After a reaction time of 3.5 h, workup and column chromatography gave a 53% yield of 6-methyl-6-(*p*-anisyl)fulvene, a bright orange solid, mp 64.0–65.5 °C. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C,84.30; H, 7.19.

**6-Methyl-6-(*p*-tolyl)fulvene** was obtained from *p*-methylacetophenone (0.300 mol) in 18% yield as a dark red liquid but was purified by vacuum distillation [bp 126.0–128.5 °C (7 mm)]. MS, *m/e* 182 ($M^+$), 167 ($M - CH_3$).

**6-Methyl-6-(*p*-fluorophenyl)fulvene** was obtained as a red-orange oil in 63% yield from 0.084 mol of *p*-fluoroacetophenone. MS, *m/e* 186 ($M^+$, $C_{13}H_{11}F$), 171 ($M - CH_3$).

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**6-Methyl-6-(*p*-chlorophenyl)fulvene** was obtained as a viscous, dark orange liquid in 56% yield from 0.084 mol of *p*-chloroacetophenone. MS, *m/e* 207, 205 ($M^+$, $C_{13}H_{11}Cl$).

**6-Methyl-6-(*p*-bromophenyl)fulvene.** Reaction of *p*-bromoacetophenone (0.084 mol) with cyclopentadiene afforded a 68% yield of 6-methyl-6-(*p*-bromophenyl)fulvene as a dark orange, viscous oil. MS, *m/e* 246 ($M^+$, $^{79}Br$), 248 ($M^+$, $^{81}Br$), 233 and 231 ($M^+ - CH_3$), 167 ($M^+ - Br$).

**6-Methyl-6-(*p*-acetylphenyl)fulvene** was prepared by reaction of *p*-diacetylbenzene (0.074 mol) with 1 equiv of monomeric cyclopentadiene, as described above, for 45 min. Chromatography (silica gel; $CH_2Cl_2$ eluant) afforded 3.1 g (20%) of product as an orange powder, mp 90.0–91.5 °C. Anal. Calcd for $C_{15}H_{14}O$: C, 85.67; H, 6.71. Found: C, 85.07; H, 6.99. MS, *m/e* 210 ($M^+$), 195 ($M - CH_3$), 167 ($M - CH_3CO$).

**6-Methyl-6-(*p*-cyanophenyl)fulvene.** Reaction of 0.069 mol of *p*-cyanoacetophenone with an equimolar amount of cyclopentadiene for 1.5 h gave 6-methyl-6-(*p*-cyanophenyl)fulvene as an orange oil in 36% yield. MS, *m/e* 193 ($M^+$), 178 ($M - CH_3$).

**Acknowledgment.** We gratefully acknowledge the technical assistance of Doris LaSpina and Fred Carter in the early stages of this work, and of Professor George Vogel, who ran the mass spectra for us.

**Registry No.** 6-Methyl-6-phenylfulvene, 2320-32-3; 6-methyl-6-(*p*-aminophenyl)fulvene, 91158-21-3; 6-methyl-6-(*p*-tolyl)fulvene, 38069-02-2; 6-methyl-6-(*p*-chlorophenyl)fulvene, 13347-54-1; 6-methyl-6-(*p*-anisyl)fulvene, 38069-03-3; 6-methyl-6-(*p*-fluorophenyl)fulvene, 78405-51-3; 6-methyl-6-(*p*-bromophenyl)fulvene, 32884-56-3; 6-methyl-6-(*p*-acetylphenyl)fulvene, 91158-22-4; 6-methyl-6-(*p*-cyanophenyl)fulvene, 91158-23-5; 6-(*p*-aminophenyl)fulvene, 91158-24-6; 6-(*p*-hydroxyphenyl)fulvene, 91158-25-7; 6-(*p*-tolyl)fulvene, 32884-55-2; 6-phenylfulvene, 7338-50-3; 6-(*p*-chlorophenyl)fulvene, 32884-54-1; cyclopentadiene, 542-92-7; *p*-aminoacetophenone, 99-92-3; *p*-methoxyacetophenone, 100-06-1; *p*-methylacetophenone, 122-00-9; *p*-fluoroacetophenone, 403-42-9; *p*-chloroacetophenone, 99-91-2; *p*-bromoacetophenone, 99-90-1; *p*-diacetylbenzene, 1009-61-6; *p*-cyanoacetophenone, 1443-80-7.

# Iron-Containing Metallophosphazenes and Their Clusters Derived from Chlorophosphazenes and Organometallic Dianions[1]

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**Abstract:** Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, reacts with disodium octacarbonyldiferrate, $Na_2Fe_2(CO)_8$, to yield the diiron and triiron cyclotriphosphazene complexes **2** and **3**, respectively. The analogous cyclic tetramer $(NPCl_2)_4$ reacts similarly to yield the diiron and triiron analogues **5** and **6**, respectively. Compounds **2** and **5** are the first *chlorophosphazenes* that contain two metal–phosphorus covalent bonds and a three-membered spirocyclic ring at phosphorus. Compound **3** can also be obtained by the thermal reaction of **2** with the neutral carbonyl complexes $Fe(CO)_5$ and $Fe_2(CO)_9$. In addition, the thermal reaction of **2** with $Ru_3(CO)_{12}$ yields the mixed-metal cluster **7**, similar in structure to **3**, but with a $Ru(CO)_3$ unit in place of the nitrogen-bound $Fe(CO)_3$. The trimetallic clusters **3**, **6**, and **7** are the first phosphazene compounds in which a portion of the phosphazene ring has been incorporated into a metallic cluster unit. Compounds **3**, **6**, and **7** contain both phosphorus–metal and nitrogen–metal bonds, demonstrating both the covalent and coordinative capacities of phosphazene rings. The new metallophosphazenes were characterized by $^{31}P$ NMR, Mössbauer, infrared, and mass spectral techniques and by X-ray crystal structure analyses.

The synthesis and characterization of new metal cluster compounds, and especially mixed-metal clusters, have attracted wide attention.[2] These species are of interest as new catalysts or catalyst precursors and have been examined as models for catalytic metal surfaces.[3] Our interest in this area stems from the realization that cyclic phosphazenes are potentially versatile multifunctional "ligands" for the stabilization of transition-metal compounds. Although a few transition-metal-linked phosphazenes have already been reported, this area remains relatively unexploited.

Several of the known examples of transition-metal-bound phosphazenes are adducts in which the skeletal nitrogen atoms function as electron-rich donors, especially when electron-supplying alkylamino and alkyl substituent groups are present.[4-11] For example, platinum dichloride complexes have been prepared via coordinative bonding to the lone-pair electrons on the backbone nitrogen atoms in aminophosphazenes of formula $[NP(NHCH_3)_2]_n$, where $n = 4$ or 15000.[tt]

A number of complexes have also been prepared by the attachment of transition metals to pendent donor groups linked to either cyclic or high polymeric phosphazenes. These include phosphino,[12-14] *nido*-carboranyl,[15] acetyleno,[16,17] and ferrocenyl side groups.[18,19] The interactions of metal carbonyl compounds

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