ment; one is an ionic mechanism (a)[10] and the other (b) involves two consecutive sigmatropic 1,5 shifts. A mechanistic study is now underway.

Acknowledgment. We thank Mr. K. Sasaki for performing the double resonance experiments.

(10) The similar ionic mechanism has been postulated for the isomerization of the spiro[2.6]nona-2,4,6-triene derivative to the indane derivative: T. Mukai, T. Nakazawa, and K. Isobe, *Tetrahedron Lett.*, 565 (1968); W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **92**, 6391 (1969).

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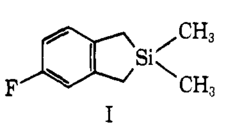
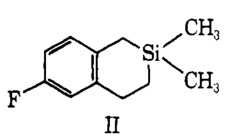
Stereoelectronic Dependence of Metallomethyl Substituent Effects by Fluorine-19 Nuclear Magnetic Resonance

Sir:

Fluorine-19 substituent chemical shifts (scs) indicate that metallomethyl groups are electron releasing relative to the methyl group when disposed para to fluorine in the benzene ring system,[1,2] a phenomenon which was first revealed by chemical reactivity and spectroscopic studies.[2,3] This metallomethyl substituent effect has been explained in essentially three different ways, either by: (i) an inductive effect, (ii) hyperconjugation, or (iii) a combination of i and ii.

Since it is expected that $\sigma-\pi$ conjugation would have similar stereoelectronic requirements to p-π conjugation[3,4] we have sought to evaluate the relative importance of the two mechanisms in the ground state by determining whether fluorine-19 chemical shifts show any dependence on the geometrical relationship of the carbon-metal bond and the π system of the aromatic substrate. Accordingly, we have synthesized three bicyclic silicon compounds (I, II, and III), together with the appropriate carbon analogs (5-fluoroindan and 6-fluorotetralin), in which the C-Si bond is constrained to a varying degree to the nodal plane of the adjacent π system.


I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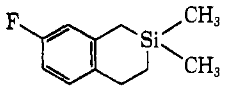
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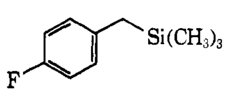
IV

If the inductive effect is more important, then the chemical shift for I and II relative to 5-fluoroindan and 6-fluorotetralin, respectively, should be comparable to the shift observed for IV relative to *p*-fluorotoluene (+1.57 ppm in cyclohexane; +1.75 ppm in DMF),[1c] while if the hyperconjugative mechanism is predominant then the relative chemical shifts for I and II should be significantly less positive (C-Si σ bond less electron donating) than +1.57 or +1.75 ppm in the appropriate solvent.[5,6]

The results shown in Table I seem to provide a fairly definite answer to the problem. First of all, it can be seen from the chemical shifts of I and II relative to the shifts of the appropriate carbon analogs (+0.24 and +0.84 ppm in cyclohexane; +0.21 and +1.16 ppm in DMF) that the electron-donating ability of the C-Si bond (indicated by the degree of shielding of the fluorine nucleus) is conformationally dependent. Since the π-inductive effect is expected to be insensitive to angular effects of this type, these results are clearly in accord with a predominant $\sigma-\pi$ interaction. It is of interest to note that the relative shift of II (+1.16 ppm in DMF) is approximately what one would expect on the basis that the hyperconjugative interaction is a function of cos θ, where θ is the angle of twist (cos 40° $\simeq$ 0.76).[6-8]

Table I. ^{19}F Chemical Shifts in Hz and (ppm) Relative to TCTFB in Cyclohexane and DMF

Compound	Solvent[a] Cyclohexane	DMF
I[b]	+236 (+4.19)	+318 (+5.64)
II[b]	+283 (+5.02)	+377 (+6.69)
III[b]	+198 (+3.51)	+288 (+5.10)
5-Fluoroindan[c]	+223 (+3.95)	+306 (+5.43)
6-Fluorotetralin[c]	+236 (+4.18)	+312 (+5.53)

[a] The fluorine nmr spectra were measured with a Varian A56/60 operating at 56.4 MHz using solutions containing 15% (w/w) of the fluoro compound, together with 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB). [b] I, II, and III gave satisfactory analyses and their proton nmr spectra were in accordance with the assigned structures; details will be given in a main paper. [c] Available from another investigation (see ref 9 and W. Adcock, P. D. Bettess, and S. Q. A. Rizvi, *Aust. J. Chem.*, **23**, 1921 (1970).

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(1) (a) W. Adcock, B. F. Hegarty, W. Kitching, and A. J. Smith, *J. Organometal. Chem.*, 12, 21 (1968); (b) W. Kitching, W. Adcock, and B. F. Hegarty, *Aust. J. Chem.*, **21**, 2411 (1968); (c) A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, **92**, 6140 (1970).

(2) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometal. Chem.*, 20, 49 (1969), and references therein.

(3) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 7476 (1970), and references therein; (b) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, **93**, 5715 (1971); (c) J. M. Jerkunica and T. G. Traylor, *ibid.*, **93**, 6278 (1971).

(4) (a) R. S. Mulliken, *J. Chem. Phys.*, 7, 339 (1939); R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, **63**, 41 (1941); (b) A. N. Nesmeyanov and I. I. Kritskaya, *Dokl. Akad. Nauk SSSR*, **121**, 447 (1958); (c) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(5) This assumes, to a first approximation, that the relative importance of CH and CC hyperconjugation is indistinguishable. Since no definitive experimental distinction has yet been made this seems reasonable.

(6) An examination of Dreiding models shows that to a first approximation it can be assumed that I and 5-fluoroindan are planar molecules and that the C–Si bond in the former does not interact significantly with the π system. In II, III, and 6-fluorotetralin the alicyclic ring is conformationally mobile, there being two freely interconvertible conformations. However, whereas in 6-fluorotetralin the interconversion is between two half-chair conformations, both II and III seem to favor half-boat forms. In fact, the models for II and III cannot be maintained in a half-chair conformation. The dihedral angle between the C–C–Si plane and the aromatic ring in the half-boat arrangement is ~50° for II and III suggesting that any hyperconjugative interaction between the C–Si bond and the π system should be significantly reduced compared to IV, but greater than in I where the dihedral angle is = 0°.

(7) M. J. S. Dewar, *J. Amer. Chem. Soc.*, 74, 3345 (1952). The resonance integral β^{θ} is given approximately by $\beta^{\theta} \simeq \beta^{0} \cos\theta$, where θ is the angle of twist.

(8) Eaborn and coworkers (see ref 2) have indicated that a maximum C–Si hyperconjugative interaction is achieved in the phenyl system with the $(Me_3Si)_2CH$ group which has a scs 2.13 ppm (CCl_4) upfield from the scs of the CH_3 substituent.

Secondly, the small upfield shift of I relative to 5-fluoroindan (+0.24 and +0.21 ppm) in cyclohexane and DMF, respectively, together with the downfield shift of III relative to 6-fluorotetralin (−0.67 ppm in cyclohexane; −0.43 ppm in DMF) suggests that the inductive field effect of the C–Si bond is extremely small. In fact, the relative downfield shift of III is opposite to what is expected from simple inductive effects emanating from the electropositive silicon. Although it is tempting to attribute the origin of the downfield shift to the likely formal positive charge residing on the carbon atom adjacent to fluorine (due to alternating polarization of the π system), recent experimental results indicate that ^{19}F chemical shifts in structurally similar aryl fluorides are sensitive to geometrical distortion.[9] The chemical-shift difference between III and 6-fluorotetralin undoubtedly reflects a conformational subtlety between the two systems.[6,10]

The conclusions from this study are in agreement with the recent proposals of Eaborn and coworkers[2] and Traylor and coworkers.[3] Our recent suggestion[1c] that the large "hyperconjugative σ–π" interaction of metallo substituents in the neutral ground state is due to the inductive effect (field and π-inductive effects) needs reappraisal along the present lines. Our work in this area continues.

Acknowledgment. We are extremely grateful to Dr. I. Rae of Monash University for his services in obtaining the ^{19}F nmr spectra and are grateful to the Australian Research Grants Committee for their partial support of this work.

(9) W. Adcock, J. Alste, and M. A. Zeb, unpublished work.

(10) An inspection of Dreiding models shows that whereas the benzylic hydrogens in 6-fluorotetralin (half-chair) are staggered around 8 H, they are eclipsed in III (half-boat) leading to "peri-like" interactions as in naphthalene.

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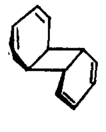
A Directed Synthesis of *cis-anti-cis*-Tricyclo[6.4.0.0^{2,7}]dodecatetraene (*o,o'*-Dibenzene). Thermal Rearrangement of a Blocked Dibenzene to a Caged (CH)$_{12}$ Precursor[1]

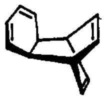
Sir:

There is special interest in the cycloaddition dimers of benzene, a subset of the (CH)$_{12}$ series,[2] because the concerted thermal dissociations of the *anti-o,o'*, *syn-o,o'*, and *p,p'* isomers **1a**, **1b**, and **2** to two molecules of benzene are "forbidden" by orbital symmetry, but that of the *o,p'* isomer **3** is "allowed."[3] The rates of dissociation therefore could provide an estimate of the magnitude of the orbital symmetry forces in a cycloreversion reaction. The first preparation of a member of this series is due to Schröder, who found the *anti-o,o'* dimer **1a** (9% yield) among the thermal transformation products of [12]annulene.[2e,f,h,i,4] We report here a directed synthesis of **1a** by a method which affords the hydrocarbon free of side products and which, because of a new rearrangement developed en route, may be adaptable to the syn isomer **1b** and other (CH)$_{12}$ compounds.

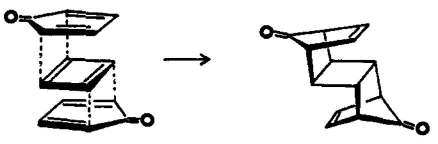

1a


1b


2


3

The key step in each of two synthetic approaches we have studied is the unmasking of a disguised cyclohexadiene system. Conceptually, the first route involves the construction of a precursor of the tricyclic skeleton by addition of two cyclopentadienone equivalents to a cyclobutadiene unit to give **4**. The synthetic steps consist of KO-*t*-Bu–Me$_2$SO dehydrohalogenation of the dimethoxytetrachlorocyclopentadienone (DMTC)–3,4-dichlorocyclobutene adduct[6] to a pentachlorodiene,[7] dechlorination to the tricyclic ketal **5**,[7] Diels–Alder addition of another mole of DMTC followed by dechlorination to **6**,[7] and hydrolysis to the volatile, crystalline diketone **4**.[7]


4

Pyrolysis of **4** (102° in C$_6$D$_5$NO$_2$) or photolysis (2537 Å, −15°, a temperature at which **1a** is thermally stable[2e,f,h,i]) give only benzene and CO. Whether **1a** is an intermediate in these reactions cannot be stated with confidence, since it undergoes pyrolytic and photochemical cycloreversion to benzene under the above conditions more readily than diketone **4** decarbonylates.

Pyrolysis of **4** in the presence of excess dimethylacetylene dicarboxylate suppresses the formation of benzene and gives the diadduct **7** of **1a**, identified by

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(1) This work was supported in part by grants from the National Science Foundation (GP 11017X) and the Hoffmann-La Roche Foundation.

(2) For references to examples of (CH)$_{12}$, see (a) G. Schröder and W. Martin, *Angew. Chem., Int. Ed. Engl.*, **5**, 130 (1966); (b) G. Schröder, *ibid.*, **2**, 481 (1963); (c) J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, *J. Amer. Chem. Soc.*, **89**, 612 (1967); (d) L. A. Paquette and J. C. Stowell, *ibid.*, **93**, 5735 (1971); *Tetrahedron Lett.*, 4159 (1969); (e) H. Röttele, W. Martin, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **102**, 3985 (1969); (f) G. Schröder, W. Martin, and H. Röttele, *Angew. Chem., Int. Ed. Engl.*, **8**, 69 (1969); (g) E. Le Goff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969); (h) J. F. M. Oth, H. Röttele, and G. Schröder, *Tetrahedron Lett.*, 61 (1970); (i) J. F. M. Oth, J. M. Gilles, and G. Schröder, *ibid.*, 67 (1970).

(3) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970; (b) *cf.* also D. Bryce-Smith, *J. Chem. Soc. D.*, 806 (1969).

(4) Dibenzene **1a** is a plausible but at present not obligatory intermediate in the formation[5] of its maleic anhydride (MA) bisadduct or benzene from the action of NaI on 3,6,9,12-tetramethanesulfonoxytricyclo[6.4.0.0^{2,7}]dodeca-4,10-diene in the presence or absence of MA, respectively.

(5) E. H. Gold and D. Ginsburg, *J. Chem. Soc. C*, 15 (1967).

(6) M. Avram, I. G. Dinulescu, G. H. D. Mateescu, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **13**, 505 (1966).

(7) All new substances reported had the correct molecular composition by either combustion analysis (Alfred Bernhardt) or high-resolution mass spectrometry (for which we thank Dr. W. J. McMurray of the Division of Health Science Resources at Yale).