support for the model. Some predictions based on considerations of the t_1–s contributions to polarization, and on the general treatment, are of interest. (1) The t_1–s contribution to polarization of products obtained by trapping of radicals which have undergone diffusive separation from the critical pairs is in the *same* direction as that of the products arising from radical pair collapse. (The t_0–s contribution is opposite.) (2) The t_1–s contribution to polarization does not depend on the existence of kinetic processes which compete with collapse of the critical pairs to products. This removes one of the barriers to the observation of polarization from reactions of short-chain diradicals, so even if the prediction of Closs and Trifunac[3] that these cannot lead to t_0–s polarization is correct, there still may be a chance to observe t_1–s polarization.

Another feature of t_1–s polarization is that a difference in g values of the radicals of the critical pairs is not necessary for energy polarization. Thus, one may observe polarizations from reactions at low fields which might not give any polarizations when carried out in high fields.

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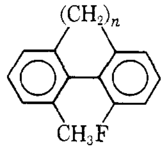
Long-Range Proton–Fluorine Spin–Spin Coupling in Bridged Biphenyls. Compelling Evidence for a "Through-Space" ("Direct") Mechanism

Sir:

Although many "through-space" ("direct"[1]) proton–fluorine,[2] fluorine–fluorine,[3] and to a lesser extent, proton–proton[4] spin–spin couplings have been claimed or discussed in recent years, truly unequivocal examples of such interactions are rare indeed.

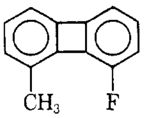
To provide compelling evidence for through-space contributions to spin–spin coupling mechanisms one needs to study systems where the internuclear distance between the interacting nuclei can be incrementally varied while keeping other variables (bond angles, dihedral angles, substituent effects, etc.) approximately constant.[2g] These systems should also be conformationally rigid so that the internuclear distances between the coupling nuclei can be determined confidently with suitable models.

We now wish to disclose our preliminary studies involving proton (methyl)–fluorine coupling over six bonds (${}^6J_{CH_3,F}$) in the bridged-biphenyl system A. This system was selected for study because the compounds in the series would seem to precisely satisfy the aforementioned criteria for assessing the importance of through-space coupling and the requirements for its existence.[5]



A

The first two members of the bridged-biphenyl series A (n = 0, 1), 1-fluoro-8-methylbiphenylene (**1**) and 4-fluoro-5-methylfluorene (**2**), have been synthesized and their nmr spectra recorded. **1** was prepared in a conventional manner.[6] An Ullmann copper-coupling reaction[7] between 2-iodo-3-nitrotoluene[8] and 2-fluoroiodobenzene gave 2-methyl-2′-fluoro-6-nitrobiphenyl (yellow-orange oil, 29%). This was catalytically reduced to 2-methyl-2′-fluoro-6-aminobiphenyl (colorless oil, 79%) which was diazotized and converted to 2-methyl-2′-fluoro-6-iodobiphenyl (amber oil, 66%). This in turn was oxidized[6] and converted to the corresponding iodonium iodide (mp 142–144° dec, 49%) which afforded 2-methyl-2′-fluoro-6,6′-diiodobiphenyl (mp 83–84°, 99%) on heating with commercial cuprous oxide. When this diiodobiphenyl was subsequently heated with freshly prepared cuprous oxide,[9] 1-fluoro-8-methylbiphenylene (**1**) was obtained (colorless oil, 27%) along with starting material. Heating the iodonium iodide with freshly prepared cuprous oxide afforded **1** in 74% yield. **1** was conveniently characterized as the 2,4,7-trinitrofluorenone 1:1 complex[10] (mp 173–174°) and could be regenerated in a pure state by passing the complex through alumina. Similarly, **2** was pre-



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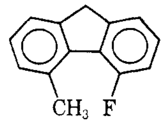

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(5) As methylene groups are inserted between the ortho positions of the biphenyl system (*i.e.*, A) the methyl and fluorine will be forced closer together for $n \leqslant 2$, as viewed with Dreiding models.

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pared in a standard fashion.[11] Methyl 2-iodo-3-methylbenzoate[12] and 2-fluoroiodobenzene were subjected to the Ullmann reaction[7] to give, after saponification, 2-methyl-2′-fluoro-6-carboxybiphenyl (amber oil, 76%), which, without purification, was heated with polyphosphoric acid to afford 4-fluoro-5-methylfluorenone (**3**) (mp 149–150°, 34%). A Wolff–Kishner reduction of this ketone gave 4-fluoro-5-methylfluorene (**2**) (mp 37°, 27%). **2** was also conveniently characterized as the 2,4,7-trinitrofluorenone 1:1 complex (mp 184°) and could be regenerated in a pure state by passing the complex through alumina.

The proton nmr spectrum of **1** (60 MHz, $CDCl_3$) shows a sharp singlet at 2.12 ppm[13] and a multiplet centered at 6.48 ppm in the anticipated ratio of 1:2. These absorptions are assigned to the methyl group[14] and the aromatic protons, respectively. In stark contrast to **1**, the proton nmr spectrum of **2** (60 MHz, $CDCl_3$) exhibits a *doublet* at 2.73 ($|J| = 8.3$ Hz),[15] a broad singlet at 3.85, and a multiplet centered at 7.18 ppm in the anticipated ratio of 3:2:6. These absorptions are assigned to the methyl, methylene, and aromatic protons, respectively. Clearly, the methyl group in **2** must be coupled to the fluorine atom, six bonds away. This is the largest $^{6}J_{HF}$ yet observed, from the few examples known.[16]

Because of the lack of observable splitting in **1** and because of the gross similarity between **1** and **2** *except* for the CH_3–F internuclear distance,[17] ~2.84 Å in **1** and ~1.44 Å in **2**, we feel that the evidence is overwhelmingly in favor of a dominant through-space (direct) contribution to the coupling mechanism in **2**.[18] As might be expected, the sum of the van der Waals radii of hydrogen and fluorine (~2.55 Å) lies between the measured internuclear H–F distance for **1** and **2**.

The long-range splitting is also observed for derivatives of **2**: 4-fluoro-5-methylfluorenone (**3**), $|^{6}J_{CH_3,F}| = 7.3$ Hz; 4-fluoro-5-methylfluoren-9-ol (**4**), $|^{6}J_{CH_3,F}| = 7.8$ Hz; 4-fluoro-5-methyl-9-chlorofluorene (**5**), $|^{6}J_{CH_3,F}| = 8.1$ Hz; and 4-fluoro-5-methyl-9-acetoxyfluorene (**6**), $|^{6}J_{CH_3,F}| = 7.8$ Hz.[19] These values are roughly in accord with increased coupling as the internuclear distance decreases. The shorter C–C bonds to the bridging atom in ketone **3** (sp^2) result in an increased separation of methyl and fluorine (measured distance ~1.60 Å). Likewise, the electronegative substituents in **4**, **5**, and **6** should enrich the per cent s character in the bridging bonds relative to **2**, increasing the CH_3–F distance and leading to smaller values of $|J_{CH_3,F}|$, as observed. Due to the substantial electronic difference between **2** and **3**, it might also be argued that if a significant "through-bond" contribution was present then a larger difference in the methyl–fluorine couplings between **2** and **3** than 1 Hz would be observed.

This system and related ones would appear to be ideal for the study of other long-range couplings and nuclear Overhauser effects. Our work in this area continues.[20]

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(15) The proximity of the fluorine in **2** is reflected in the unusually low-field absorption of the methyl protons.

(16) The previously observed largest $^{6}J_{HF}$ appears to be 3.8 Hz.[2h]

(17) The proton–fluorine closest approach distance as measured with Dreiding models.

(18) A through-bond contribution is expected to be small in any event: $|^{6}J_{CH_3,F}|$ in *p*-fluorotoluene is 0.9 Hz; R. E. Richards and T. Schaefer, *Trans. Faraday Soc.*, **54**, 1447 (1958).

(19) The observed splitting is field independent: $|^{6}J_{CH_3,F}| = 7.3$ Hz at 100 MHz ($CDCl_3$) for **3**.

(20) All new isolated compounds gave satisfactory combustion analyses and/or mass spectra, and all new compounds exhibited nmr and infrared spectra in accord with their assigned structures.

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Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. II. Application to the Synthesis of Semibullvalene[1]

Sir:

Recent developments have given evidence that molecules endowed with highly strained σ bonds can interact sufficiently strongly with certain metallic reagents to experience skeletal rearrangements not directly available to them under ordinary conditions because of orbital symmetry restrictions. Of the various agents known to effect such valence isomerizations, silver(I) ion is rapidly emerging as a unique catalyst, in the sense that interaction of its atomic orbitals with a given set of σ bonds apparently leads to concerted bond rearrangements.[1–3] In contrast, rhodium-on-carbon and coordination complexes of rhodium seem to promote isomerizations by way of nonconcerted carbon–carbon bond insertion mechanisms.[4] We wish now to describe an extension of our earlier work on silver(I) ion catalyzed rearrangements of 1,1′-bishomocubyl systems[1] to the synthesis of semi-

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