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Dependence of Through-Space ^1H–^{19}F Coupling on Molecular Geometry in 9-Alkyl-1,2,3,4-tetrafluorotriptycene Derivatives

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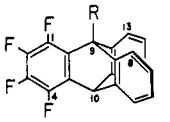
In a series of 9-alkyl-1,2,3,4-tetrafluorotriptycenes, the 1-fluorine nucleus couples with some of the α- and β-protons in the 9-substituent, especially with those located in the ±*sc* sites with respect to 1-F, suggesting that the coupling occurs through-space. The coupling to β-protons in a ±*sc*-methyl group (6.2–9.0 Hz) depends on the molecular geometry of each derivative and is correlated with the distance between the fluorine and the methyl carbon atoms. In 9-*sec*-alkyl but not in 9-*tert*-alkyl derivatives, the β-protons in the *ap*-methyl group show a significant coupling with 1-F (0.9–1.0 Hz). The magnitude of the coupling between 1-F and α-protons of the 9-substituent is independent of the location of the α-proton, indicating that the H–F coupling occurs not only when the relevant nuclei are in proximity but also when the fluorine and the C–H bond adopt a nearly linear arrangement, allowing the orbitals of the fluorine and the carbon atoms to overlap.

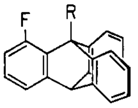
Triptycene derivatives have proved to be an excellent system for the investigation of rotational isomerism and related phenomena by means of NMR spectroscopy.[1] Because of the rigidity of the triptycene skeleton and the high rotational barrier around the bridgehead-to-substituent bond, a substituent at a peri position (1, 8, or 13 in 1) and a group attached to the α-carbon of the 9-substituent can be forced to reside in close proximity to each other for a time long enough to be observed by NMR spectroscopy. This has allowed the study of a variety of intramolecular interactions in a series of triptycene derivatives.[2-5] We report here on long-range spin–spin couplings between the fluorine nucleus at the peri position and the α- or β-protons of the 9-substituent in a series of 9-alkyl-1,2,3,4-tetrafluorotriptycene derivatives (1–8) and some related compounds and discuss their dependence on molecular geometry.



	R
1	$C(CH_3)_3$
2	$C(CH_3)_2CN$
3	$C(CH_3)_2CH_2C_6H_5$
4	$CH(CH_3)_2$
5	$CHCH_3OCH_3$
6	CH_3
7	CH_2CH_3
8	$CH_2C_6H_5$

Results and Discussion

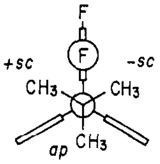
^1H NMR spectral data are compiled in Tables I–III. In many spectra an additional splitting, ascribable to a spin–spin coupling with a single fluorine nucleus, is observed. Although direct evidence from heteronuclear decoupling experiments is not available, the following facts identify the coupling partner. The ^1H NMR spectra of 3 and 4 display almost the same spectral pattern as those of their monofluoro counterparts 9[6] and 10,[7] respectively.



9 R = $C(CH_3)_2CH_2C_6H_5$
10 R = $CH(CH_3)_2$

This suggests that the fluorine atom at the 1-position is responsible for the observed H–F coupling in 3 and 4. It is reasonable that the same is true for the other tetrafluoro derivatives and is supported by the ^{19}F NMR spectra of the tetrafluoro compounds. The multiplets assigned to the 2-, 3-, and 4-F nuclei can be simulated without H–F couplings, while the 1-F signal appearing as an ill-resolved complex multiplet at lowest field is not reproduced by such simulations, indicating the presence of coupling with protons.[8,9]

In 1, where the internal rotation about the C_9–C_α bond is slow, the *tert*-butyl protons give rise to three equally intense signals corresponding to a six-proton doublet at δ 2.02 (J = 7.5 Hz) and a three-proton singlet at δ 2.08. The doublet is unequivocally assigned to the ±*sc*-methyl groups and the singlet to the *ap*-methyl (Newman projection 11). The ±*sc*-methyl protons show a large six-bond H–F coupling of 7.5 Hz, while the *ap*-methyl protons couple with at most 0.2 Hz, suggesting that a through-bond mechanism is unimportant for the latter. Molecular models show that the internuclear distance between the 1-fluorine and the ±*sc*-methyl carbon is about 2.4 Å,



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[1] Ōki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 87; *Top. Stereochem.* **1983**, *14*, 1.

[2] Suzuki, F.; Ōki, M. *Tetrahedron Lett.* **1974**, 2845; *Bull. Chem. Soc. Jpn.* **1975**, *48*, 596.
Suzuki, F.; Ōki, M. *Tetrahedron Lett.* **1974**, 2845; *Bull. Chem. Soc. Jpn.* **1975**, *48*, 596.

[3] Ōki, M.; Izumi, G.; Yamamoto, G.; Nakamura, N. *Chem. Lett.* **1980**, 213; *Bull. Chem. Soc. Jpn.* **1982**, *55*, 159.

[4] Izumi, G; Yamamoto, G.; Ōki, M. *Chem. Lett.* **1980**, 969; *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3064.

[5] Yamamoto, G.; Tanaka, Y.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3028.

[6] Yamamoto, G.; Suzuki, M.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 306.

[7] Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2082.

[8] Details of the ^{19}F NMR spectra of these compounds will be discussed elsewhere.

[9] Appearance of the bridgehead proton (10-H) signal as a doublet is therefore ascribed to the coupling with the 1-fluorine, which is in line with the recent finding by Gribble and Kelly[10] that the 8-fluorine couples with the 4-proton in 8-fluoro-1-methyl-1,4-dihydronaphthalene 1,4-endoxide but the 5-fluorine does not couple with the 4-proton in the corresponding 5-fluoro compound.

[10] Gribble, G. W.; Kelly, W. J. *Tetrahedron Lett.* **1981**, *22*, 2475.

0022-3263/84/1949-1913$01.50/0

Table I. ^{1}H NMR Data of *9-tert*-Alkyltriptycenes in CDCl$_3$[a]

compd	rotamer	β-protons *ap*-CH$_3$	β-protons ±*sc*-CH$_3$	β-protons CH$_2$	10-H
1		2.08 s	2.02 d (*7.5*)		5.64 br d (*1.6*)
2	*ap*		2.41 d (*6.3*)		5.77 br d (*1.8*)
	±*sc*	2.43 s	2.39 d (*7.0*)		5.73 br d (*1.8*)
3	*ap*		2.04 d (*9.0*)	3.88 s	5.74 br d (*1.6*)
	±*sc*	2.09 s	1.95 d (*8.3*)	3.61 br d (14.1), 3.97 dd (14.1, *2.4*)	5.72 br d (*1.6*)
9	*ap*		2.06 d (*8.4*)	3.90 s	5.27 br d (*1.8*)
	±*sc*	2.10 s	1.97 d (*7.9*)	3.77 br d (14.4), 3.96 dd (14.4, *2.1*)	5.27 br d (*1.8*)

[a] Signals due to aromatic protons are omitted. Chemical shifts are given in δ; s, singlet; d, doublet, dd, double doublet; br d, broad doublet. In parentheses are coupling constants in hertz. Those in italics are couplings with ^{19}F.

Table II. ^{1}H NMR Data of 9-*sec*-Alkyltriptycenes in CDCl$_3$[a]

compd	rotamer	population, %	α-protons *ap*-H	α-protons ±*sc*-H	β-protons *ap*-CH$_3$	β-protons ±*sc*-CH$_3$	10-H	OCH$_3$
4	*ap*	10	3.62 d sep (6.8, *2.4*)			1.75 app t (6.8, *6.2*)[b]	*c*	
	±*sc*	90		3.77 d sep (6.8, *2.4*)	1.76 dd (6.8, *0.9*)	1.84 app t (6.8, *6.2*)[b]	5.71 d (*1.8*)	
10	*ap*	10	3.58 d sep (6.7, *2.0*)			1.81 dd (6.7, *5.8*)	*c*	
	±*sc*	90		3.82 d sep (6.8, *2.0*)	1.80 dd (6.8, *0.9*)	1.85 dd (6.7, *5.8*)	5.26 d (*1.6*)	
5	*ap*	39		5.19 dq (5.9, *2.9*)		2.05 dd (5.9, *7.1*)	5.69 d (*1.5*)	3.73 s
	*sc**(*S**)	55		5.16 dq (6.0, *1.6*)	2.00 dd (6.0, *1.0*)		5.71 d (*1.5*)	3.6. d (*0.9*)
	*sc**(*R**)	6	5.01 dq (5.9, *2.7*)			1.99 dd (5.9, *7.4*)	*c*	3.71 s

[a] Signals due to aromatic protons are omitted. Chemical shifts are given in δ; s, singlet; d, doublet; app t, apparent triplet; dd, double doublet; dq, double quartet; d sep, double septet. In parentheses are coupling constants in hertz. Those in italics are couplings with ^{19}F. [b] The H–F coupling constant was calculated assuming a vicinal coupling constant of 6.8 Hz. [c] Unidentified because of the small population.

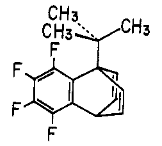
Table III. ^{1}H NMR Data of 9-*prim*-Alkyltriptycenes in CDCl$_3$[a]

compd	α-protons *ap*-H	α-protons ±*sc*-H	β-protons *ap*-CH$_3$	β-protons ±*sc*-CH$_3$	10-H
6	2.56 d (*5.6*)				5.77 d (*1.9*)
7	3.19 dq (7.0, *3.0*)		1.63 dt (7.0, *3.3*)		5.71 d (*1.8*)
19	4.27 dq (15.0, 6.8)	3.47 ddq (15.0, 6.8, *2.4*)		1.52 dt (6.8, *3.9*)	5.59 d (*2.0*)
8	4.65 d (*2.8*)				5.83 d (*1.5*)

[a] Signals due to aromatic protons are omitted. Chemical shifts are shown in δ; d, doublet; dt, double triplet; dq, double quartet; ddq, double double quartet. In parentheses are coupling constants in hertz. Those in italics are couplings with ^{19}F.

shorter than the sum of the van der Waals radii of fluorine and carbon, and hence the existence of a through-space mechanism is reasonable.[11-13]

A similar long-range coupling of 2.9 Hz occurs between 8-F and the ±*sc*-methyl protons in 1-*tert*-butyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (**12**).[15] The larger coupling in **1** is ascribed to the enhanced proximity of the relevant nuclei in **1** caused by the buttressing of the two *o*-benzeno bridges.



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In 2[16] and 3,[17] where two stable atropisomers, *ap* and ±*sc*, are isolated, the signals due to the *ap*-methyl protons appear as sharp singlets, while the ±*sc*-methyl signals show H–F couplings ranging from 7.0 to 9.0 Hz. The variations may reflect small differences in the distances between the fluorine atom and the methyl groups. As shown in Scheme

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(11) Hilton, J.; Sutcliffe, L. H. *Progr. NMR Spectrosc.* **1975**, *10*, 27.

(12) The internal rotation of a methyl group is usually very fast on the NMR time scale and the H–F coupling exhibited by the three protons of a methyl group is the average of the three couplings. Therefore, in discussing the magnitude of the H–F coupling exhibited by a methyl group, we refer to the internuclear distance between the fluorine and the methyl carbon rather than to the individual distances between the fluorine and the three protons or to their average.

(13) Myhre et al. presented a correlation between the fluorine–methyl proton coupling constants and the internuclear distances between the fluorine and the methyl carbon atoms.[14] According to the correlation the distance of 2.4 Å corresponds to a coupling constant of ca. 7 Hz, in good agreement with the present finding, although the data used by Myhre et al. are based on five-bond couplings.

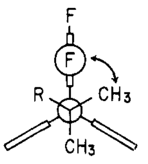
(14) Myhre, P. C.; Edmonds, J. W.; Kruger, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 2459.

(15) Brewer, J. P. N.; Heaney, H.; Marples, B. A. *Chem. Commun.* **1967**, 27. Brewer, J. P. N.; Eckhard, I. F.; Heaney, H.; Marples, B. A. *J. Chem. Soc. C* **1968**, 664.

(16) Yamamoto, G.; Tanaka, A.; Suzuki, M.; Morita, Y.; Ōki, M.; *Bull. Chem. Soc. Jpn.* **1984**, *57*, 891.

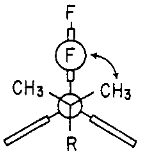
(17) Yamamoto, G.; Suzuki, M.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 809.

Scheme I



13

	R	J_{HF}/Hz
±*sc*-**4**	H	6.2
±*sc*-**2**	CN	7.0
1	CH_3	7.5
±*sc*-**3**	$CH_2C_6H_5$	8.3



14

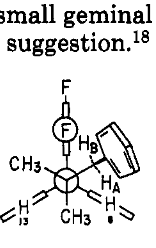
	R	J_{HF}/Hz
ap-**4**	H	6.2
ap-**2**	CN	6.3
1	CH_3	7.5
ap-**3**	$CH_2C_6H_5$	9.0

I, the bulkier the group R is in **13** and **14**, the larger the coupling constant becomes.

In **13**, an increase in the bulk of R may induce torsion about the axis bond, causing the ±*sc*-methyl group to approach the fluorine. The fluorine–methyl distance in **14** should decrease as R becomes bulkier because C_α is buttressed to the fluorine and/or because the CH_3–C–CH_3 angle decreases.

In ±*sc*-**3**, the methylene protons as well as the ±*sc*-methyl protons couple with 1-F. The methylene protons are diastereotopic and appear primarily as an AB-type quartet at δ 3.61 and 3.97 with a geminal coupling constant of 14.1 Hz. The low-field half shows a further splitting of 2.4 Hz. The high-field half appears as a broadened doublet, whereas irradiation of the *ap*-methyl proton signal at δ 2.09 reveals an additional coupling of 1.8 Hz.

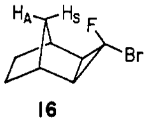
Molecular models suggest that the benzylic phenyl group orients antiperiplanar to the triptycyl moiety, adopting a conformation in which the benzene ring is perpendicular to the bisecting plane of the methylene group, as shown in **15**. The relatively small geminal coupling constant of 14.1 Hz supports this suggestion.[18]



15

The low-field methylene proton at δ 3.97 is assigned to H_A in **15** from a nuclear Overhauser effect experiment; upon irradiation of the lowest field one-proton multiplet at δ 8.14, assigned to 8-H flanking the benzyl group, the low-field half of the methylene multiplet is enhanced by about 20% while the other half remains unchanged. The high-field methylene proton at δ 3.61 is therefore assigned to H_B. The presence of a small unresolved long-range coupling between H_B and the *ap*-methyl protons is consistent with the assignment because the relevant nuclei can adopt the favorite W arrangement.

From this assignment it is evident that 1-F couples not only with the proximate H_B but also with the remote H_A and that the magnitude of the coupling is larger for the remote H_A. A similar situation is encountered[19] in **16**, the fluorine coupling not only with H_S (3.6 Hz) but also with H_A (3.0 Hz), although in **16** the coupling to H_S is larger than to H_A. It was suggested that, for the H_A–F coupling, the coupling information might be transmitted by way of the H_S atom or by an interaction with the back-lobe of the H_A–C bond orbital.[19] The same explanation may apply to **3**. We infer that the large H_A–F coupling in ±*sc*-**3** is an example of the importance of overlap of the fluorine and carbon orbitals in transmitting spin-state information. Another example will be presented in a later section.



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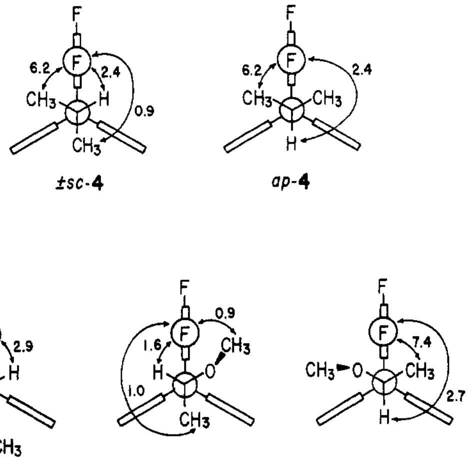
Scheme II



In compounds **4** and **5**, with a secondary group at the bridgehead position, all possible rotamers about the axis bond are evident in the NMR spectra.[20] In each rotamer of these compounds, the signal of the ±*sc*-methyl protons is identified by an H–F coupling of 6.2–7.4 Hz (Table II and Scheme II). Interestingly, the signal assigned to the *ap*-methyl group in ±*sc*-**4** or *sc**(*S**)-**5** is split by 0.9–1.0 Hz, ascribed to a coupling with 1-F because the monofluoro compound **10** behaves like **4**. We would like to suggest for these couplings that the spin information of 1-F nucleus is transmitted through-space and then through-bond to the *ap*-methyl protons by way of the C_α–C_{ap} orbital. Absence of similar couplings in 9-*tert*-alkyl derivatives may be due to steric reduction of the interaction between 1-F and the α-carbon.[21]

It is also intriguing that the magnitude of the H_α–F couplings in these compounds is insensitive to the location of the α-proton. In the 9-isopropyl derivative **4** and also in **10**, the H_α–F couplings are independent of the rotamers. In the 9-(1-methoxyethyl) compound **5**, the H–F coupling decreases in the order *ap* > *sc**(*R**) > *sc**(*S**), unrelated to the H–F distance. Therefore, 1-F couples not only with the proximate ±*sc* proton but also with the remote *ap* proton, a similar phenomenon to that observed in ±*sc*-**3** above. The interaction between a lone-pair orbital on the 1-fluorine atom and the back-lobe of the C_α–H_{ap} bond orbital may therefore be important for the H_{ap}–F coupling.

Another interesting aspect is that the methoxyl protons couple with 1-F in the *sc**(*S**) rotamer of **5**. Absence of the coupling in *ap*-**5** is reasonable because the methoxyl

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(18) Barfield, M.; Grant, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 1899.

(19) Jefford, C. W.; Hill, D. T.; Ghosez, L.; Toppet, S.; Ramey, K. C. *J. Am. Chem. Soc.* **1969**, *91*, 1532.

(20) Tanaka, Y.; Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3023.

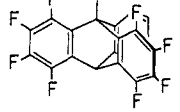
(21) Change in the geometrical situation like this is found in the X-ray crystallographic data of 1,2,3,4-tetrachlorotriptycene derivatives with primary and tertiary substituents at the bridgehead: Mikami, M.; Toriumi, K.; Konno, M.; Saito, Y. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2474; Nogami, N.; Ōki, M.; Sato, S.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3580.

Table IV. Yields, Melting Points, and Analytical Data

compd	yield, %	mp, °C	found (%) C	found (%) H	found (%) Cl	calcd (%) C	calcd (%) H	calcd (%) Cl
1	37	238–240	75.26	4.65		75.38	4.74	
4	23	187–188	74.93	4.21		74.99	4.38	
6	32	152–153	74.33	3.38		74.12	3.55	
7	24	161–162	74.84	3.88		74.57	3.98	
8	57	207–208	77.70	3.71		77.88	3.87	
19	20	209–210	62.22	2.72	16.84	62.43	2.86	16.75

group is too remote from 1-F. The difference in the behavior between *sc**(*S**)-**5** and *sc**(*R**)-**5**, in both of which the methoxyl group resides in a ±*sc* site flanking 1-F, may be explained as follows. The dihedral angle of CH_3–O–C–CH_3 will be somewhat larger than 60° in any of the rotamers because of the steric repulsion between the methyl groups. Then the distance between the methoxyl carbon and the fluorine will be smaller in *sc**(*S**)-**5** than in *sc**(*R**)-**5** as shown in the Newman projections in Scheme II, resulting in the H–F coupling in *sc**(*S**)-**5** only.[22]

In **6**–**8**, carrying a primary alkyl group at the bridgehead position, the internal rotation about the axis bond is fast at room temperature, and only averaged spectra are observed. The methyl proton signal of **6** appears as a doublet with an H–F coupling of 5.6 Hz. This value may be compared with 5.95 Hz in **17**[23] and 5.1 Hz in **18**.[15] This trend may be explained by the change in the distance between the peri fluorine(s) and the methyl carbon atom.



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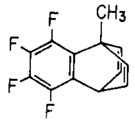
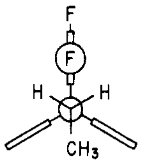
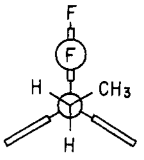


18

The ^1H and ^{19}F spectra of **7** display rotamer-averaged signals at room temperature. The ^{19}F spectrum of **7** at −45 °C indicates almost equal amounts of the *ap* and ±*sc* rotamers.[24] The ^1H NMR spectrum of **7**, however, shows broad signals for the methyl and methylene protons even at −60 °C, probably because of the small chemical shift differences between the rotamers, and thus gives no direct information on the magnitude of the H–F couplings in the individual rotamers. We can estimate the F–CH_3 coupling in ±*sc*-**7** as 5.6 Hz, taking into account the observed mean of 3.3 Hz, the almost equal populations of the two rotamers, and assuming that the magnitude in *ap*-**7** is 1.0 Hz, a similar value to those found in **4** and **5**. The estimated value of 5.6 Hz is slightly smaller than those found in **1**–**5**.



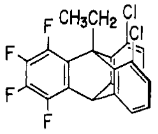
ap-**7**



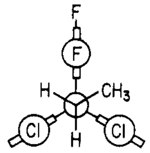
±*sc*-**7**

The H–F couplings for the methylene protons in **7** and **8** are half those for the methyl protons in **6**. The population-weighted average of the α-proton coupling constants in **4** and **5** are 2.4 and 2.2 Hz, respectively, which are even smaller than that in **7**.

To obtain individual H–F couplings in a rotamerically frozen 9-ethyl compound, we studied **19**. The ^1H NMR spectrum of **19** shows that the compound exists solely as the ±*sc* rotamer (**20**). The methylene protons are anisochronous, appearing at δ 3.47 (J_{gem} = 15.0, J_{vic} = 6.8, and J_{HF} = 2.4 Hz) and at δ 4.27 (J_{gem} = 15.0 and J_{vic} = 6.8 Hz, somewhat broadened). The low-field signal is assigned to H_{ap} because it is flanked by two deshielding chlorine substituents. The width of the peaks suggests that the H_{ap}–F coupling is not larger than 1.5 Hz. The methyl protons couple to fluorine by 3.9 Hz, considerably smaller than the estimated value for ±*sc*-**7**. This is contrary to the expectation that the coupling constant should be larger in **19** than in ±*sc*-**7** because the *peri*-chloro groups would buttress the methyl group toward the 1-fluorine. This anomaly is not understood.



19



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We have presented several examples of long-range H–F couplings to which a through-space mechanism seems to make a significant contribution. β-Methyl protons in a ±*sc* site couple strongly to 1-F, while those in an *ap* site do not in 9-*tert*-alkyl derivatives. However, they exhibit a small coupling in 9-*sec*-alkyl derivatives and present an interesting problem about the coupling mechanism. As for the α-protons, for which the orientation of the C–H bond relative to the coupling fluorine nucleus is firmly defined, the H–F coupling is apparently independent of the internuclear distance between the proton and the fluorine atom. This fact reveals that there are at least two stereochemical situations where significant H–F through-space couplings are observed. One is the proximity of the atoms containing the fluorine and the proton, and the other is the quasi-linear arrangement of the fluorine atom and the C–H bond in which the fluorine lone-pair orbital can interact with the back-lobe of the C–H bond. A similar phenomenon is observed for the diastereotopic β-methylene protons in ±*sc*-**3**. As for the H–F couplings exhibited by methyl protons, both pathways should contribute to the observed coupling. An experimental verification is not available because of the fast internal rotation of a methyl group.

Experimental Section

Spectral Measurements. ^1H NMR spectra were obtained on a Varian EM-390 spectrometer at 90 MHz as chloroform-*d* solutions at a temperature of ca. 35 °C with tetramethylsilane as internal lock. Chemical shifts were calibrated with a Hew-

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[22] Molecular mechanics calculations by Dr. Kazuhisa Abe, Yokohama National University, actually reproduce the situation. Details of the calculations will be published elsewhere. Abe, K., private communication.

[23] Hankinson, B.; Heaney, H.; Sharma, R. P. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2372.

[24] Two peaks at 16.9 and 19.7 ppm downfield from the internal hexafluorobenzene, which are assigned to 1-F of *ap*-**7** and ±*sc*-**7**, respectively, coalesced into a single peak at 18 ± 3 °C, the free energy of activation for the *ap* → ±*sc* conversion being 13.8 ± 0.2 kcal mol^{-1}.

J. Org. Chem. **1984**, *49*, 1917-1925

lett-Packard 5381A frequency counter and are shown in δ. Coupling constants were obtained by a first-order analysis of the spectra and are reliable to ±0.2 Hz. Some of the ^1H spectra were also recorded on a Hitachi R-20B spectrometer at 60 MHz so as to aid the spectral assignments.

Materials. Syntheses and characterizations of triptycenes **2**,[16] **3**,[17] **5**,[20] **9**,[6] and **10**[7] are described elsewhere. 9-Methyl-,[25] 9-ethyl-,[25] 9-benzyl-,[26] 9-isopropyl-,[27] and 9-*tert*-butylanthracene[28] were prepared as described in the literature. Preparation of 1,8-dichloro-9-ethylanthracene is described elsewhere.[29]

General Procedure for the Synthesis of Tetrafluorotriptycenes. To a boiling solution of 1.5 mmol of 9-alkylanthracene and 0.5 mL of isopentyl nitrite in 30 mL of dichloromethane was added dropwise a solution of 3.0 mmol of tetrafluoroanthranilic acid[30] in 20 mL of tetrahydrofuran during the course of 1 h, and the mixture was heated under reflux for 1 h. After evaporation of the solvent, the residue was chromatographed through an alumina column with hexane containing 5% of benzene as the eluent. The fractions containing the desired triptycene were usually contaminated with a considerable amount of the corresponding 1,4-adduct, 9-alkyl-1,2,3,4-tetrafluoro-5,12-dihydro-5,12-ethenonaphthacene, which was removed by fractional crystallizations from tetrahydrofuran–hexane. Yields, melting points, and analytical data of the triptycenes are compiled in Table IV.

Registry No. **1**, 89657-23-8; **2**, 89657-24-9; **3**, 73524-75-1; **4**, 89657-25-0; **5**, 88473-97-6; **6**, 89657-26-1; **7**, 89657-27-2; **8**, 89657-28-3; **9**, 86194-40-3; **19**, 89657-29-4; 3,4,5,6-tetrafluoroanthranilic acid, 1765-42-0.

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Rearrangements of Ylides Generated from Reactions of Diazo Compounds with Allyl Acetals and Thioketals by Catalytic Methods. Heteroatom Acceleration of the [2,3]-Sigmatropic Rearrangement

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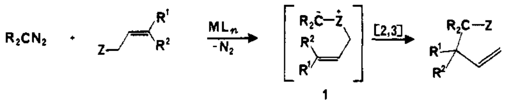
Allyl acetals undergo ylide generation in rhodium(II) acetate catalyzed reactions with diazo esters with subsequent production of 2,5-dialkoxy-4-alkenoates by the [2,3]-sigmatropic rearrangement in moderate to good yields. The synthetic versatility of this class of polyfunctional compounds has been examined with selected transformations. Cyclopropanation and Stevens rearrangement compete with the [2,3]-sigmatropic rearrangement in certain cases, and the influence of reactant structure and reaction conditions on this competition is reported. Comparative results with allyl ethers, which undergo cyclopropanation almost exclusively, demonstrate that heteroatom substitution on the allylic carbon accelerates ylide rearrangement. With dithioketals such as 2-ethenyl-2-methyl-1,3-dithiane, the ylide generated from $Rh_2(OAc)_4$ catalyzed reactions of ethyl diazoacetate undergoes [2,3]-sigmatropic rearrangement in competition with intramolecular elimination but without evidence of either cyclopropanation or Stevens rearrangement. Only when the [2,3]-sigmatropic rearrangement cannot occur competitively does the Stevens rearrangement become important in reactions with dithioketals. In these examples the catalytic methodology for ylide generation is advanced as an attractive alternative to base promoted methodologies.

We have previously reported that $Rh_2(OAc)_4$ and $Rh_6(CO)_{16}$ catalyzed reactions of diazo compounds with a broad selection of allylic substrates result in products of the [2,3]-sigmatropic rearrangement of intermediate allylic ylides (eq 1).[1] Allylamines, sulfides, and iodides give the corresponding sigmatropic rearrangement product exclusively, whereas allyl bromides and chlorides undergo catalytic cyclopropanation in competition with ylide formation and rearrangement. In the series of allyl chloride, bromide, and iodide, allyl iodide gave the highest and allyl chloride the lowest yield of ylide-derived product. The extent of ylide generation through reaction of an allyl halide with an electrophilic metal carbene is consistent with the relative nucleophilicities of halides,[2] but C–Z bond strengths may also contribute to the effectiveness of these sigmatropic rearrangements.



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(1)

Although the catalytic methodology for ylide generation is applicable to the general classification of allylic substrates, its most advantageous use is in the preparation of allylic ylides that are not amenable to generation by the base-promoted methodologies.[3] However, the relative ability of heteroatoms such as oxygen[4] or chloride[1] to stabilize free ylides such as **1** has been disappointing. Cyclopropane formation is the dominant product-forming process with these allylic substrates. To compensate for

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