The Complete Analysis of the ^{19}F Nuclear Magnetic Resonance Spectrum of Octafluorostyrene

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Summary A complete analysis of the ^{19}F n.m.r. spectrum of the eight-spin octafluorostyrene system is presented.

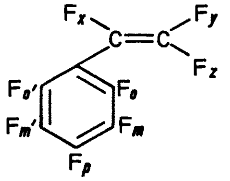
A PARTIAL analysis of the ^{19}F n.m.r. spectrum of octafluorostyrene has appeared previously,[1] but only the chemical shifts, the three vinyl J_{FF}'s, and three of the nine vinyl-ring J_{FF}'s were reported. As can be seen from the Table, the present work constitutes a complete analysis of this eight-spin system.

We have determined by direct analysis the magnitudes of all the J's and the relative signs of J_{om} and $J_{om'}$. Tickling experiments removed all remaining ambiguities regarding relative signs of J's and the assignment of the values of 6·1 and 0·7 Hz to $J_{oo'}$ and $J_{mm'}$ respectively. In this way it was possible to pick out the correct combination of signs and assignments among the 2^{16} likely cases. No assumptions on relative signs were made, except that J_{om} and $J_{om'}$ have different signs (from the direct analysis of the aa'xx' subspectra) and that the ^{0}J's (J_{om} and J_{mp}) have like signs. Since much redundancy was involved in the results of the tickling experiments, there is no doubt of the validity of the analysis.

This work appears significant in three ways. (i) For the first time relative signs of ring-vinyl J_{FF}'s have been obtained. (ii) These signs could be related to intra-ring and intra-vinyl J_{FF}'s, and since the signs of the latter have been related to that of $^{1}J_{CH}$, which can be taken as absolutely positive,[2] the absolute signs of all the J_{FF}'s studied here could be established. In particular, the signs of the $^{0}J_{FF}$'s turned out to be negative. (iii) This last result leads to the conclusion that $^{0}J_{HH}$'s are positive, since it has been shown earlier[3] that $^{0}J_{FF}$'s and $^{0}J_{HH}$'s have opposite signs.

Because so little on vinyl–ring J_{FF}'s is known, not much can be said at present as to their meaning for the interpretation of the coupling mechanisms involved. However, a trend is observed in the magnitudes of the vinyl–(*ortho, meta, para*) J_{FF}'s which is similar to that in benzylic–(*ortho, meta, para*) J_{HH}'s:[4] the magnitudes of the coupling constants with *meta* nuclei are the smallest of the three types in both series.

^{19}F *N.m.r. parameters of octafluorostyrene*



Larmor frequencies (Hz) at $\nu = 94{\cdot}1$ MHz
(referred to 1,2-dichlorotetrafluorocyclobutene)

Ring	Vinyl
$\omega_o = +\ 1785$	$\omega_x = +\ 4926$
$\omega_m = +\ 4083$	$\omega_y = -\ 2055$
$\omega_p = +\ 2953$	$\omega_z = -\ \ 561$

Coupling constants (Hz)

Intra-vinyl	Intra-ring	Ring–vinyl
$J_{xy} = +\ 35{\cdot}4$	$J_{om} = -20{\cdot}0$	$J_{ox} = +\ 7{\cdot}1$
$J_{xz} = -118{\cdot}3$	$J_{op} = +\ 4{\cdot}0$	$J_{oy} = +\ 2{\cdot}2$
$J_{yz} = +\ 62{\cdot}5$	$J_{om'} = +\ 8{\cdot}5$	$J_{oz} = +10{\cdot}4$
	$J_{oo'} = -\ 6{\cdot}1$	$J_{mx} = -\ 0{\cdot}8$
	$J_{mm'} = -\ 0{\cdot}7$	$J_{my} = +\ 0{\cdot}2$
	$J_{mp} = -19{\cdot}0$	$J_{mz} = -\ 0{\cdot}4$
		$J_{px} = +\ 3{\cdot}2$
		$J_{py} = +\ 0{\cdot}8$
		$J_{pz} = +\ 1{\cdot}5$

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[2] *Cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Pergamon Press, New York, 1966, p. 888.

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[4] *Cf.* S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.