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(9) (a) O. S. Tee and S. Banerjee, Can. J. Chem., 52, 451 (1974); (b) S. Banerjee, M.S. Thesis, Sir George Williams University, 1972.
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Fluorine-19 Nuclear Magnetic Resonance Studies of Nitrogen-Substituted Fluorobenzenes

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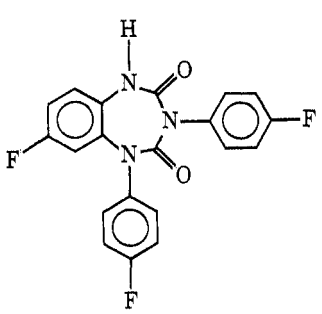
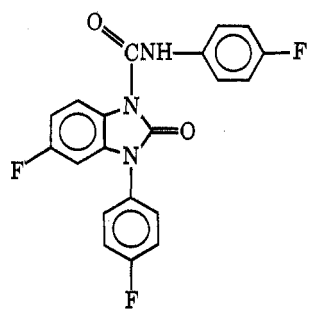
^{19}F chemical shifts of a series of nitrogen-substituted fluorobenzenes have been investigated to demonstrate their use as a probe in determining structure. σ constants are evaluated for selected nitrogen substituents from chemical shifts of the meta- and para-substituted fluorobenzenes. The results are discussed in terms of inductive, resonance, and conformational effects of the substituents on nitrogen.

Although many ^{19}F chemical shifts of fluorobenzenes with nitrogen substituents have been reported,[1-5] the appropriate model compounds required for the structure elucidation of a by-product from the reaction of nitrobenzene with carbon monoxide[6] were not available. A series of carbonyl-substituted nitrogen derivatives were compiled (Tables I and II) and analzed to show that the structure was **58a** or **58b**, but the final assignment of **58b** had to be accomplished



58a



58b

by preparing authentic samples of the nonfluorinated analogues and comparing spectral properties. In addition, we prepared and measured the ^{19}F chemical shifts for a series of meta- and para-substituted fluorobenzenes to determine σ constants for a number of nitrogen functions not previously reported.

Results and Discussion

In Table I the meta- and para-^{19}F chemical shifts for a series of nitrogen-substituted fluorobenzenes are reported relative to fluorobenzene. For this series, Taft's inductive and resonance parameters, σ_I and σ_R,[1] are calculated and compared to literature values. Although this is not a complete compilation of substituent effects for nitrogen functions from ^{19}F shift measurements, it is comprehensive and includes much new data. Table II gives the ^{19}F NMR chemical shifts of a further series of para-nitrogen-substituted fluorobenzenes. The data in Table I are arranged in order of increasing inductive power of the substituent (downfield shift of *m*-fluorine) in contrast to Table II which emphasizes the resonance effects.

Oxygen Bonded to Nitrogen (ArNO). The *p*-fluoro resonance for nitrobenzene (**34**) appears at very low field because the large resonance withdrawal effect of nitro reinforces its strong inductive withdrawal effect. However, the *p*-fluoro shift for nitrosobenzene (**17**) is slightly further downfield although the nitroso group is inductively less effective (expected from the electronegative substitution by one vs. two oxygens). Steric factors may inhibit the resonance interaction of nitro relative to nitroso. The azoxyphenyl group [–N(O)=NAr, see **25**] has an inductive effect intermediate between nitroso (NO) and nitro (NO_2) as expected from replacement of one oxygen by the less electronegative NAr group. The resonance interaction of this group is less than nitro or nitroso ($\sigma_R \sim +0.06$ vs. +0.21 for nitro and +0.32 for nitroso; note that the *p*-fluoro shifts in azoxybenzenes have not been definitely assigned but are not significantly different) as would be expected if the bulky ArN group inhibits coplanarity required for effective resonance interaction.

Nitrogen Substituents of Nitrogen (ArNN). The *p*-fluoro shifts for both the phenylhydrazine **3b** and hydrazobenzene **40** are only slightly downfield from aniline. Both fluorines in azoxybenzene **25** are very similar, and close to *cis*-azobenzene rather than the trans isomer. The ammonium cation (see **35**) has almost no effect on the *p*-fluoro resonance, whereas the resonance effect of the diazonium ion (see **39**) shifts its resonance to the lowest field of all fluoroaromatic compounds.

The meta shifts move downfield in order NH_2, NHOH, N=NAr (trans), N=N(→O)Ar, N=NAr (cis), –N=O. The cis form of azobenzene **22** has an inductive effect larger than the =N(→O)Ar group (assuming the assignment indicated for the *m*-fluoro shifts for the azoxybenzene). Direct interaction of the π system of the phenyl groups may occur in the cis isomer causing this unusual downfield shift. The resonance effects suggest that the phenyl groups must be twisted and the N=N system cannot effectively conjugate to withdraw charge density from the ring [σ_R(cis) −0.04 vs. σ_R(trans) +0.08, see Figure 1]. In the cis form, resonance donation of charge density (Figure 1) may become the major factor. Such electron donation by resonance has been proposed for arylazoplatinum compounds.[7a] Our conclusions on the cis and trans structures are supported by other experimental evidence.[7b]

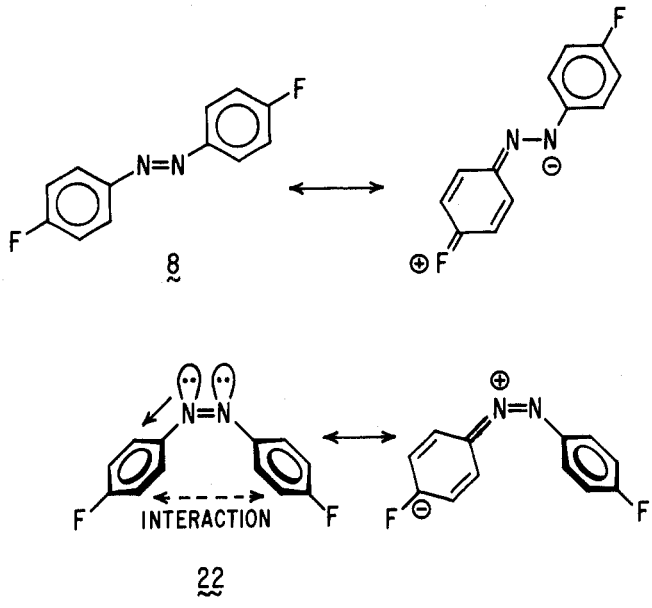
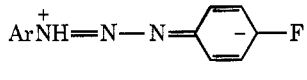


Figure 1. Resonance interactions of *cis*- and *trans*-azobenzenes.

Only one para ^{19}F resonance is seen for diphenyltriazene **52** owing to rapid proton exchange. The triazene anion **41** shows a singlet at slightly higher field. In 1-methyl-1-phenyl-3-(4-fluorophenyl)triazene (**55**) the single resonance may be similar to the corresponding resonance in the parent compound **52.** Simple arithmetic predicts the second reso-

$C_6H_5NN{=}NAr$	$ArNHN{=}NAr$
CH_3	
−117.0	$(-120.6 - 117.0)/2 = -118.8$
55	**52**

nance in the parent compound to be about −120.6. The marked upfield shift (−117) of the triazene **55** relative to that of azobenzene (δ −110) **8** may arise from a resonance interaction involving the nitrogen as shown. The downfield shift

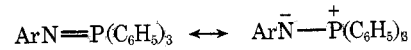


of the other resonance relative to phenylhydrazine **3** (−120.6 vs. −125) is similarly explained. The utility of the fluorinated triazenes in structural studies of transition metal complexes has been discussed.[7c]

Two resonances are seen for *N*-nitrosobis(4-fluorophenyl)amine (**27**), demonstrating that rotation about the N–N bond and inversion at nitrogen is slow. The fluorine chemical shift difference of 4 ppm is extremely large for rotational isomers at so remote a position, but the available data do not allow unambiguous assignment of the resonances to their respective rings.

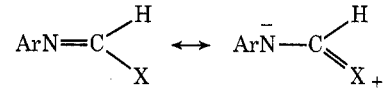
The effect of nitrogen substitution on a nitrogen substituent should be contrasted with a recent report of phosphorus substitution on nitrogen.[14] The $N{=}P(C_6H_5)_3$ group (see compound **0,** Table I) appears to be the most electron-donating group on record. A very strong inductive electron donation (σ_I −0.20) is enhanced by a strong resonance donation (σ_R −0.45). Although the ressonance donation is slightly less effective than a NH_2 group, the strong inductive effect makes the $N{=}P(C_6H_5)_3$ group the strongest electron-donating group that has been measured.

The electron-donating ability of the $N{=}P(C_6H_5)_3$ group suggests a large contribution from the ylide resonance structure. The aminyl anion ^-NR should be one of the most pow-



erful electron-donating groups, and since the electronegativity of phosphorus is close to that of hydrogen, the phosphinimines are probably a reasonable model for the anilide anion Ar^-NH.

Nitrogen Bonded to Carbon. A. ArN=C. The *p*-fluoro shifts for isocyanate **18** and carbodiimide **16** are quite close, suggesting little resonance difference between these groups. The isocyanate group is inductively a little stronger because of the greater electronegativity of the C=O compared to C=NAr. The *p*-fluoro shift differences between various types of imines are very significant, suggesting large and variable resonance contributions from ionic forms.

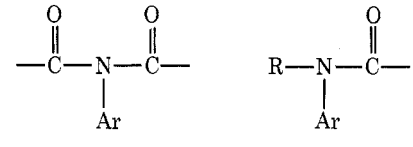


X	Compd	−δ
C_6H_5	**54**	117.5
OC_2H_5	**47**	120.4
$N(CH_3)_2$	**42**	123.9

The isonitrile group (see compound **30**) is inductively more electron withdrawing than nitroso, suggesting that an electron-deficient carbon is more electronegative than oxygen. However, the isonitrile does not accept the charge by resonance nearly as effectively as a nitroso group since the σ_R of −N≡C is only +0.02 vs. +0.30 for nitroso.

B. ArNC=O. Because of our interest in products derived from phenyl isocyanate, this class of compounds is the largest of those we studied. The *p*-fluoro shifts of ureas and urethanes occur at highest field in the −121-ppm range. Substitution at the three position of ureas (compounds **6** and **7**) causes little shift of the one aryl resonance unless there is also a conformation change (see compound **46a**). Amides have a slightly lower field *p*-fluoro resonance in the range of −119 ppm. The shift differences between various types of amides is less than 1 ppm and, in general, shifts from isomeric amides can be resolved though not assigned.

The *p*-fluoro shifts of N,N-disubstituted compounds, of which imides are a special case, appear at low field in the range



of −113 ppm. The shift ranges for imides and N,N-disubstituted amides overlap so much that these classes cannot be distinguished by ^{19}F NMR (see below). Thus we could not predict the positions of the ^{19}F NMR resonances of **58a** and **58b** with sufficient accuracy to unambiguously assign the correct structure to the then unknown product.[6] Phenyl substitution on nitrogen causes a 5-ppm downfield shift, independent of the remaining substitution. Compare amines **1, 9,** and **19** and ureas **7** and **46b.**

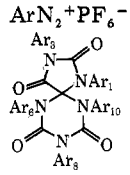
The meta shifts also vary considerably, and again both substitution and configuration have significant effects. Two striking examples are the effect of a 5-aryl substituent in the biurets **10** and **24** in producing a marked upfield shift.

The data for the isocyanate groups and their dimers and trimers should be compared with those of the related bisamide and biuret in Table I. The isocyanate trimers **15** have chemical shifts and σ parameters similar to those of the bisamides **23** and the biurets **51.** The two carbonyl functions on the nitrogen make the nitrogen electron withdrawing inductively and damp

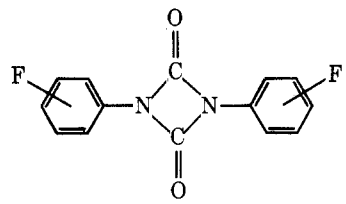
Table I. ^{19}F NMR Chemical Shifts of Nitrogen Substituted Fluorobenzenes and Substituent Parameters

	Compd (Ar = C_6H_4F)	Chemical shift, ppm[a] $\int_H^m$	$\int_H^p$	$\int_m^p$	Substituent parameters σ_I	σ_R	Solvent	Ref
0	$ArN{=}P(C_6H_5)_3$	+2.02	+15.45	+13.43	−0.20	−0.46	$CDCl_3$	14
1	$ArNH_2$	+0.50	+14.20	+13.70	+0.01	−0.48	CCl_4	1
2	$ArN(CH_3)_2$	−0.08	+15.65	+15.73	+0.10	−0.54	CCl_4	1
3a	ArNHOH	−0.27	+11.11	+11.38	+0.12	−0.39	CH_3CN	
3b	$ArNHNH_2$	−0.38	+12.25	+12.63	+0.14	−0.43	Meta in CCl_4, para in CH_3OH	1
4	$ArNHCNHC_6H_5$ (O)	−0.50	+8.55	+9.05	+0.15	−0.31	Acetone	
5	$ArN{=}NC_6H_5$ (trans)	−0.78	−3.25	−2.47	+0.19	+0.08	CCl_4	1, *b*
6	$ArNHCNH_2$ (O)	−0.78	+8.21	+8.99	+0.19	−0.30	CH_3CN	
7	ArNHCNHAr (O)	−0.96	+7.58	+8.54	+0.22	−0.29	CH_3CN	
8	ArN=NAr (trans)	−1.06	−3.39	−2.33	+0.23	+0.08	CCl_3F	*b*
9	Ar_2NH	−1.33	+9.35	+10.68	+0.27	−0.36	CCl_3F	
10	ArNHCNHCNHAr (O, O)	−1.36	+5.86	+7.22	+0.28	−0.24	CH_3CN	
11	$ArNHCCH_3$ (O)	−1.36 (−1.42, −1.70)	+5.37 +5.15	+6.76	+0.28	−0.23	$C_2H_4Cl_2$ hydrocarbon, CCl_4	5 1
12	ArN=NAr (O↑)	−1.38 [c](−1.38	−3.84 −4.17	−2.46 −2.79	+0.28 +0.28	+0.08 +0.09)	CCl_3F	
13	ArNHCH (O)	−1.42	+4.59	+6.01	+0.29	−0.20	CH_3OH	4a
		Z form −1.40	+5.15	+6.55	+0.28	−0.22	CD_3CN	4b
		E form −1.70	+5.1	+6.80	+0.32	−0.24	CD_3CN	4b
14	$ArNHCNH_2$ (S)	−1.44	+2.50	+3.94	+0.29	−0.13	CH_3CN	3
15	$(ArNCO)_3$ (cyclic trimer)	−1.53	−1.07	+0.46	+0.30	−0.20	CH_3CN	
16	ArN=C=NAr	−1.59	+4.02	+5.61	+0.31	+0.19	CCl_3F	
17	ArNO	−1.78	−11.10	−9.32	+0.34	+0.32	CCl_4	1
		−1.86	−10.78	−8.92	+0.35	+0.30	CCl_3F	
18	ArNCO	−1.92	+3.11	+5.03	+0.35	−0.17	CCl_3F	2
19	Ar_3N	−1.97	+6.73	+8.70	+0.36	−0.29	CCl_3F	
20	ArNHCN	−2.00	+7.36	+9.36	+0.37	−0.31	CH_3CN	3
21	ArN_3	−2.02	+4.73	+6.75	+0.37	−0.23	CH_3CN	
22	ArN=NAr (cis)	−2.05	−0.85	+1.20	+0.37	−0.04	CCl_3F	
23	$ArN(CCH_3)_2$ (O)	−2.06	−0.95	+1.11	+0.37	−0.04	$ClCH_2CH_2Cl$	5
24	ArNHCNHCNH$_2$ (O, O)	−2.15	+6.39	+8.54	+0.38	−0.29	CH_3CN	
25	ArN=NAr (O↑)	−2.23 [c](−2.23	−4.17 −3.84	−1.94 −1.61	+0.40 +0.40	+0.07 +0.05)	CCl_3F	
51	$ArN(CONHAr^2)_2$	−2.23	−0.93	+1.3	+0.39	−0.04	CH_3CN	
26	ArNCS	−2.39	−0.20	+2.19	+0.42	−0.07	CCl_3F	2
27	Ar_2NNO	−2.41 [d](−2.41	+1.96 −2.17	+4.37 +0.24	+0.42 +0.42	−0.15 −0.01)	CH_3CN	
28	$ArNHSO_2CH_3$	−2.42	+3.69	+6.11	+0.42	−0.21	$ClCH_2CH_2Cl$	5
29	$ArN(SO_2CH_3)_2$	−2.56	−3.56	−1.00	+0.45	+0.04	$ClCH_2CH_2Cl$	5
30	ArNC	−2.76	−3.21	−0.45	+0.47	+0.02	CCl_3F	4
31	Ar_2NNO	[d]−2.85 (−2.85	−2.17 +1.96	+0.68 −4.81	+0.49 +0.49	−0.02 −0.16)	CH_3CN	
32	$ArN(CF_3)_2$	−2.86	−3.19	−0.33	+0.49	+0.01	CCl_3F	2
33	$(ArNCO)_2$ (cyclic dimer)	−3.01	+4.02	+7.03	+0.51	−0.24	CH_3CN	
34	$ArNO_2$	−3.45	−9.55	−6.10	+0.57	+0.21	CCl_4	1
35	$ArNH_3^+$	−3.63			+0.58		CH_3OH	1
		−5.01	−3.75	+1.26	+0.79	−0.04		*e*
36	$ArN(SO_2CF_3)_2$	−4.41	−7.29	−2.88	+0.70	+0.10	$ClCH_2CH_2Cl$	5
37	$ArN(CN)_2$	−5.75	+0.64	+6.39	+0.89	−0.22	CCl_3F	*f*
38	$ArN^+(CH_3)_3$	−5.95			+0.93		CH_3OH	1

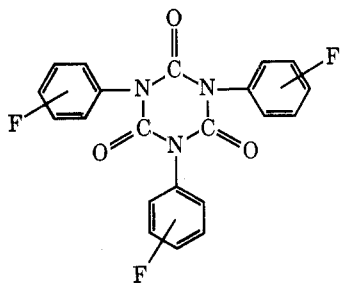
Table I (*Continued*)

	Compd (Ar = C_6H_4F)		Chemical shift, ppm[a] f_H^m	f_H^p	f_m^p	Substituent parameters σ_I	σ_R	Solvent	Ref
39	$ArN_2^+PF_6^-$		−10.28	−30.55	−20.27	+1.53	+0.69	CH_3CN	*g*
60		Ar							
		1	−4.73	−1.43	+3.3	+0.75	−0.06 ± 0.05	CH_3CN	
		3	−3.13	−2.43	+0.7	+0.52	−0.06 ± 0.05	CH_3CN	
		6,10	−3.43	−3.33	+0.1	+0.56	−0.003	CH_3CN	
		8	−1.33	−0.53	+0.8	+0.27	−0.03	CH_3CN	

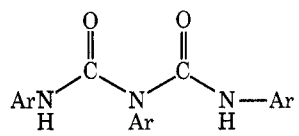
[a] Chemical shift relative to fluorobenzene (in CCl_3F, −113.10 ppm; in CH_3CN, −113.83; acetone, 113.4) using the designation (ref 1) of + to higher field. [b] A recent summary of substituent effects for the phenylazo group is given in ref 15. [c] Positive assignment of fluoroaryl was not possible. Consequently, both combinations of meta and para values are possible. Entries **12** and **25** should be compared. [d] Positive assignment of fluoroaryl was not possible. Consequently, both combinations of meta and para values are possible. Entries **27** and **31** should be compared. [e] Unpublished work by Professor Olah reported in G. A. Olah and P. R. Schleyer, "Carbonium Ions", Vol. IV, Wiley-Interscience, New York, N.Y., 1973, p 1740. [f] Unpublished data by W.A.S. and referenced in J. W. Rakskys, R. W. Taft, and W. A. Sheppard, *J. Am. Chem. Soc.*, **90**, 5236 (1968). [g] Approximate values were reported for $FC_6H_4N_2^+$ by R. W. Taft, *J. Am. Chem. Soc.*, **85**, 3152 (1963), Figure 4, as f_H^m −9.8 and f_H^p −29.8 (CH_3CN).



isocyanate dimer **33**



isocyanate trimer **15**



biuret **51**

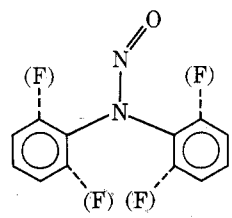
the normal resonance donation. The isocyanate dimer **33** and the isocyanate **18** both have an inductive electron-withdrawing effect (the dimer significantly more strongly), but the nitrogen remains strongly electron donating. Apparently the strain in the four-membered ring dimer makes it behave like the isocyanate rather than a nitrogen substituted by two carbonyl groups. Conformational effects as noted for *N,N'*-diarylureas[8] may also be important in these systems.

The single resonance in each of the isocyanate oligomers shows that no unsymmetrical structures are present, and provides confirmation of the structures proposed for **33** and **15**.

C. $ArNR_2$. Methyl substitution on nitrogen causes a small upfield shift, so that *N,N*-dimethyl-*p*-fluoroaniline (**2**) has a higher shift than the aniline. Electronegative groups such as cyano, trifluoromethyl, and trifluoromethylsulfonyl (see compounds **37**, **32**, and **36**) cause progressive shifts to lower field, presumably by making the nitrogen lone pair less available for resonance interaction with the aromatic ring. The *m*- and *p*-fluoro shift differences between aniline (**1**), diphenylamine (**9**), and triphenylamine (**19**) may also be explained similarly since a phenyl group is electron withdrawing, but with the additional constraint that coplanarity of even two rings is not possible because of hydrogen–hydrogen repulsions.

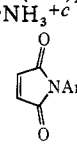
Two cyano substituents on nitrogen (compound **37**) appear very effective in making the nitrogen as electron withdrawing as if it had a full positive charge (note, however, the difference between NH_3^+ and $N(CH_3)_3^+$; see ref 1 for a discussion of this difference). However, the $N(CN)_2$ group has a σ_R of −0.22 in contrast to $N(CF_3)_2$, $N(SO_2CH_3)_2$, and $N(SO_2CF_3)_2$, which all have a positive σ_R. No obvious explanation is available other than steric interaction with the large or bulky electron-withdrawing groups prevent coplanarity needed for resonance donation of the electron pair on nitrogen and direct p–π interaction of the SO_2 or CF_3 groups gives abnormal resonance effects.

***N*-Nitrosodiphenylamines.** After observing the large chemical shift in bis(4-fluorophenyl)nitrosamine (**31**), and cognizant of the work of Randall on the ^{13}C NMR spectrum of *N*-methyl-*N*-phenylnitrosamine,[9a] we prepared the bis(3-fluorophenyl) and bis(2-fluorophenyl) analogues and observed their ^{19}F NMR spectra. If slow rotation about the *N*-phenyl bonds occurred for either of these compounds, we would expect four resonances. Only two were seen for the meta derivative. The four-line pattern of the ortho derivative arises from two resonances and an inter-ring fluorine–fluorine coupling of 3.6 Hz, δ −116.8 and −122.8. No change was seen on cooling the sample to −60 °C. Either one fluorine rotational isomer is greatly preferred or there is rapid rotation about the *N*-phenyl bond; the latter is more likely.



Use of a 4-Fluorophenyl Label in Mechanism Studies. To within the accuracy we desired for our investigation, peak heights of the proton decoupled ^{19}F NMR spectrum could be equated to mole ratios. We recognize that nuclear Overhauser effects can be quite significant, but are unlikely to vary dramatically when a para substituent is changed.[9b] The progress of a chromatographic separation is easily monitored by the changing ratio of peaks in the ^{19}F NMR spectrum. The com-

Table II. Fluorine Chemical Shifts in Nitrogen Substituted 4-Fluorobenzenes

	Compd[a]	− Chemical shift, ppm[b]		Compd	− Chemical shift, ppm
(2)	$ArN(CH_3)_2$[c]	129.7	(16)	ArN=C=NAr	117.1
(1)	$ArNH_2$	128.8	55	$C_6H_5N(CH_3)N=NAr$[e]	117.0
40	ArNHNHAr	126.9	(33)	$(ArNCO)_2$	116.8
(9)	Ar_2NH	124.1	56	$ArNHC(S)NH_2$[f]	116.6
41	ArN—N=NAr[d,e]	124.0	(18)	ArNCO	116.6
42	$ArN=CHN(CH_3)_2$	123.9	46b	$Ar_2NCONHAr$	116.0
(6)	$ArNHCONH_2$	121.8	(27)	ArN(NO)Ar	115.8
43	Ar_2NNH_2	121.6	(48)	$Ar_2NCON(Ar)CONHAr$	115.6
(20)	ArNHCN[f]	121.5	(48)	$Ar_2NCON(Ar)CONHAr$	115.3
(7)	ArNHCONHAr	121.2	(37)	$ArN(CN)_2$[h]	114.7
44	$ArNHCOOCH_3$	121.1	(35)	$ArNH_3^+$[c]	114.5
45	PhNHN(Ph)CONHAr	120.8			
(19)	Ar_3N	120.6			
46a	$Ar_2NCONHAr$	120.5	57		114.2
47	$ArN=CHOC_2H_5$	120.4			
(24)	$ArNHCONHCONH_2$	120.2			
48	$Ar_2NCONArCONHAr$	119.8		fluorobenzene	113.8
(10)	ArNHCONHCONHAr	119.7	(22)	ArN=NAr (cis)	113.0
(11)	$ArNHCOCH_3$	119.3	(51)	$(ArNHCO)_2NAr$	112.9
			(15)	$(ArNCO)_3$	112.8
(13)	ArNHCOH	119.3	(27)	ArN(NO)Ar	111.6
49	$ArNHCOCH=CH_2$	119.2	(32)	$ArN(CF_3)_2$[i]	110.9
50	$ArNHCOC_6H_5$	119.1	(30)	ArNC[j]	110.2
51	$(ArNHCO)_2NAr$	119.0	(8)	ArN=NAr (trans)	110.0
52	ArNHN=NAr[d,e]	118.8	(12)	ArN=N(O)Ar	109.2
(21)	ArN_3	118.6			108.9
53	$ArNHCOCH=CHCO_2H$	118.0[f]	(34)	$ArNO_2$[c]	103.4
54	$ArN=CHC_6H_5$	117.5	(17)	ArNO[c]	101.0
			(39)	$ArN_2^+PF_6^-$	83.3

[a] Ar is 4-fluorophenyl, Ph is phenyl. Number in parentheses is from Table I or earlier in Table II. [b] Unless indicated otherwise, chemical shift was determined at less than 5% concentration in CH_3CN relative to internal standard of CCl_3F; C_6H_5F is at −113.8 ppm under these conditions. [c] Reference 1. [d] Reference 7b, average of the two shifts. [e] In tetrahydrofuran solvent. [f] Reference 3. [g] In Me_2SO solvent. [h] See footnote *f*, Table I. [i] Reference 2. [j] Reference 4a.

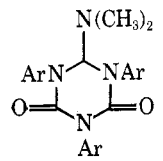
bination of broad chemical shift range with narrow absorption and the sensitivity to volatile and nonvolatile materials makes the fluorine labeling technique uniquely valuable as an analytical tool.

We have several times encountered the problem of whether or not two isomers were produced in a reaction. Gas chromatography and the ^1H NMR spectrum could not answer the question. Preparing a derivative using 4-fluorophenyl instead of phenyl provided a quick answer to the question. In all cases more than one peak was seen in the proton decoupled ^{19}F NMR spectrum, indicating a mixture of isomers. A rough quantitative analysis was possible even when the peaks could not be assigned to their respective structures. This method complements the use of ^{13}C NMR and peak counting to establish the presence of isomers, and may be the technique of choice depending on the instrumentation available.

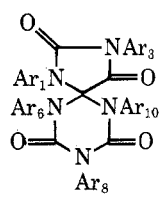
Recent examples where fluorophenyl was used as a probe to determine information on the mechanism of reactions are in studies on reactivity of intermediates from decomposition of diazodicyanoimidazole[10] and 5-diazomethyl-1,4-diphenyl-1,2,3-triazole with fluorobenzene[11] and arylbicyclooctyl cations.[12] We also used the fluorophenyl probe to study the isocyanate DMF adducts **59** and **60**.[13]

The imide and amide *p*-fluorophenyl resonances in triazine **59a** differ by less than 0.1 ppm, but when the triazinedione **59c** is prepared from a mixture of 4-fluorophenyl and phenyl isocyanates, six of the expected seven resonances for the six structures are resolved. In principle they could be assigned by preparing **59c** from various ratios of the isocyanates.

The fluorine resonances of the *m*-fluorophenyl isomer **60b** show large separations. Two resonances of spiro compounds **60a** and **60b** were assigned by reference to the mixed compounds **60c** and **60d**. However, the resonance parameters calculated from the para shifts are all small, suggesting that



59a, Ar = 4-FC_6H_4
b, Ar = C_6H_5
c, Ar = 4-FC_6H_4 or C_6H_5



60a, Ar = 4-FC_6H_4
b, Ar = 3-FC_6H_4
c, $Ar_1 = Ar_3 = C_6H_5$; $Ar_6 = Ar_8 = Ar_{10}$ = 4-FC_6H_4
d, $Ar_1 = Ar_3 = C_6H_5$; $Ar_6 = Ar_8 = Ar_{10}$ = 3-FC_6H_4
e, Ar = C_6H_5 or 4-FC_6H_4

the *N*-phenyl groups are not coplanar with the adjacent carbonyls. The same argument holds for the isocyanate trimer **15** and the central nitrogen in biuret **51**. The larger σ_R for isocyanate dimer **33** may arise because the bond angle deformation in the small ring allows the phenyl group to be coplanar with the uretidione ring. The inductive effect of one of the aryl groups on the five-membered ring is abnormal. Inspection of models suggests that in all conformations the phenyl on N-1 interacts strongly with the aryl groups in the six-membered ring. The inductive parameter for Ar_3 and isocyanate dimer

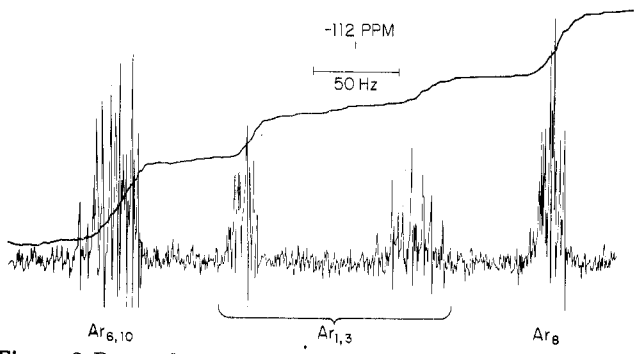


Figure 2. Proton decoupled ^{19}F NMR spectrum of **60e**.

33 are similar. The effect for Ar_8 is similar to that of the isocyanate trimer **15**, as expected for the six-membered position, but $Ar_{6,10}$ also shows an abnormally large inductive effect. Again steric interaction on $Ar_{6,10}$ could cause this apparent abnormal effect, although perhaps proximity to the spiro ring junction could create the abnormal effects for $Ar_{6,10}$ as well as Ar_1.

The immense resolving power of this fluorine labeling technique is seen in Figure 2 when the spiro compound **60e** is prepared from a mixture of phenyl and 4-fluorophenyl isocyanates. As suggested by Ulrich,[13] a statistical mixture of all possible isomers is produced. Although most unique fluorine resonances are resolved, assigning each peak to its proper isomer is essentially impossible. Changing a para hydrogen to a para fluorine has a discernible effect on a fluorine resonance as far as 15 bonds and 13 Å away.

Experimental Section

Synthesis. New compounds listed in Tables I and II were prepared by literature procedures.

NMR. ^{19}F NMR spectra were run as dilute solutions in the indicated solvents with proton noise decoupling on a Varian HA-100 instrument locked to internal $CFCl_3$.

Substituent Parameters. The inductive and resonance substituent parameters σ_I and σ_R were calculated by the procedure described by Taft et al.,[1] and as used in other substituent studies.[2-4]

$$\int_H^{m-X} = (-7.10)\sigma_I + 0.60$$

$$\int_{m-X}^{p-X} = -29.5\sigma_R$$

***N,N*-Dimethyl-*N'*-(4-fluorophenyl)formamidine (42).** A solution of 10 ml of 4-fluorophenyl isocyanate and 50 ml of DMF was heated at 115 °C overnight. Distillation at reduced pressure gave 7.5 g of colorless liquid. Anal. Calcd for $C_9H_{11}FN_2$: C, 65.0; H, 6.7. Found: C, 65.1; H, 6.9. Ir 3.4, 6.1, 6.7, 7.3, 8.2, 8.3, 9.1, 12.0, 12.9 μ; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 2.92 (s, 2 CH_3), 6.90 (d, J = 7 Hz, 4 H), 7.42 (s, =CH); ^{19}F NMR (CH_3CN/CCl_3F) δ −123.9.

1,3,5-Tris(4-fluorophenyl)-6-dimethylaminohexahydro-1,3,5-triazine-2,4-dione (59a). A solution of 2 g of imine **42** and 4 g of 4-fluorophenyl isocyanate was kept at room temperature for 2 days. The solid glass was triturated with ether to give 4.2 g of white solid, mp 161–162.5 °C. Anal. Calcd for $C_{23}H_{19}F_3N_4O_2$: C, 62.7; H, 4.4; N, 12.7. Found: C, 62.8; H, 4.5; N, 12.6. Ir 3.26, 3.39, 3.52, 3.58, 5.82, 5.96, 6.24, 6.63, 8.25, 12.15 μ; ^{1}H NMR (Me_2SO-d_6/Me_4Si) δ 3.98 (s, 2 CH_3), 6.10 (s, CH), 7.13–7.80 (m, 12 H); ^{19}F NMR (CH_3CN/CCl_3F) δ −114.53 (2), −144.44 (1).

1,3,6,8,10-Pentakis(4- and 3-fluorophenyl)-1,3,6,8,10-pentaazaspiro[4.5]decane-2,4,7,9-tetraone (60a and 60b). A solution of 2.4 g of imine **42** and 10 g of 4-fluorophenyl isocyanate was refluxed for 3 h under N_2. The viscous mass was poured into 60 ml of ether and during trituration 7.5 g crystallized. The analytical sample was recrystallized from CH_3CN, mp 249–250.5 °C. Anal. Calcd for $C_{35}H_{20}F_5N_5Oinfn4$: C, 62.8; H, 3.0; N, 10.4. Found: C, 62.6; H, 3.4. Ir 3.23, 5.53, 5.74, 5.87, 6.23, 6.61, 11.99 μ; ^{19}F NMR (CH_3CN/CCl_3F) δ −110.5 (2), −111.4 (1), −112.4 (1), −113.3 (1). The 3-fluorophenyl analogue **60b** was similarly prepared. Anal. Found: C, 63.1; H, 3.2; N, 10.4. ^{19}F NMR (CH_3CN/CCl_3F) δ −109.1 (1), −110.4 (2), −110.7 (1), −112.5 (1).

1,3-Bis(fluorophenyl)-6,8,10-triphenyl-1,3,6,8,10-pentaazaspiro[4.5]decane-2,4,7,9-tetraone (60c and 60d). A mixture of 3.9 g of **59b** and 7.5 g of 4-fluorophenyl isocyanate was heated at 150 °C overnight. Excess isocyanate was removed under vacuum and the residue triturated with acetone giving 5.5 g of white solid, mp 209 °C. Anal. Calcd for $C_{35}H_{23}F_2N_5O_4$: C, 68.3; H, 3.8; N, 11.4. Found: C, 68.5; H, 4.0; N, 11.3. ^{19}F NMR (CH_3CN/$CFCl_3$) δ −111.6, −112.7.

The 3-fluorophenyl analogue was similarly prepared, mp 214–218 °C. Anal. Found: C, 68.4; H, 3.9; N, 11.5. ^{19}F NMR (CD_3CN/$CFCl_3$) −111.3, −109.4.

Spiro Compounds 60e. A mixture of 3.6 g of phenyl isocyanate, 4.1 g of 4-fluorophenyl isocyanate, and 0.7 g of DMF was heated overnight at 150 °C under nitrogen. The glass was triturated with methanol precipitating 4.2 g of white crystals, mp 181–186 °C. The ^{1}H NMR spectrum showed only aromatic absorptions and the infrared spectrum was consistent with the spiro structure. The ^{19}F NMR spectrum is given in Figure 2. The distribution of fluoroaryl groups is not entirely random. The integral indicates an excess of this isocyanate at position 8.

Triazinediones 59c. A mixture of 3.0 g of *N,N*-dimethyl-*N'*-phenylformamidine and 5.5 g of 4-fluorophenyl isocyanate was allowed to stand at room temperature for 5 days. The viscous glass was triturated with ether precipitating 6 g of triazinedione **59c:** ^{19}F NMR ($CDCl_3$/$CFCl_3$) −113.61 (32%), −113.78 (21%), −113.79 (17%), −113.94 (19%), −113.96 (5%), and −114.07 (6%).

Registry No.—**0** para isomer, 18523-51-8; **1** para isomer, 371-40-4; **2** para isomer, 403-46-3; **3a** para isomer, 406-00-8; **3b** para isomer, 371-14-2; **4** meta isomer, 350-79-8; **4** para isomer, 330-98-3; **5** para isomer, 332-00-3; **6** meta isomer, 770-19-4; **6** para isomer, 659-30-3; **7** meta isomer, 369-83-5; **7** para isomer, 370-22-9; **8** meta isomer, 60253-47-6; **8** para isomer, 51788-93-3; **9** meta isomer, 333-53-9; **9** para isomer, 330-91-6; **10** para isomer, 60253-48-7; **11** para isomer, 351-83-7; **12,** meta isomer, 330-42-7; **12** para isomer, 326-04-5; **13** para isomer, 459-25-6; **14** para isomer, 459-05-2; **15** meta isomer, 60253-49-8; **15** para isomer, 60253-50-1; **16** meta isomer, 351-27-9; **16** para isomer, 351-74-6; **17** para isomer, 352-15-8; **18** para isomer, 1195-45-5; **19** meta isomer, 60253-410; **19** para isomer, 899-26-3; **20** para isomer, 14213-19-5; **21** para isomer, 3296-02-4; **22** para isomer, 51789-00-5; **23** para isomer, 36035-52-6; **24** para isomer, 60253-42-1; **26** para isomer, 1544-68-9; **27** meta isomer, 60253-43-2; **27** para isomer, 724-23-2; **28** para isomer, 35980-24-6; **29** para isomer, 36035-53-7; **30** para isomer, 24075-34-1; **32** para isomer, 3700-34-3; **33** meta isomer, 60253-44-3; **33** para isomer, 60253-45-4; **34** para isomer, 350-46-9; **35** para isomer, 29131-39-3; **36** para isomer, 36035-54-8; **37** para isomer, 60253-46-5; **38** para isomer, 38695-39-5; **39** meta isomer, 57103-74-9; **39** para isomer, 53260-51-8; **40** para isomer, 332-06-9; **42** para isomer, 15851-81-7; **43** para isomer, 1717-35-7; **44** para isomer, 16744-99-3; **45** para isomer, 60252-74-6; **46** para isomer, 60252-75-7; **47** para isomer, 59332-77-3; **48** para isomer, 60252-76-8; **49** para isomer, 60252-77-9; **50** para isomer, 366-75-6; **51** meta isomer, 60252-78-0; **51** para isomer, 38456-65-4; **53** para isomer, 60252-79-1; **54** para isomer, 331-98-6; **55** para isomer, 60252-80-4; **56** para isomer, 459-05-2; **57** para isomer, 6633-22-3; **59a,** 60252-81-5; **59b,** 17350-48-0; **60a,** 60252-82-6; **60b,** 60252-83-7; **60c,** 60252-84-8; **60d,** 60252-85-9.

Supplementary Material Available. The method of preparation and physical data on all new compounds, or compounds not previously well characterized in the literature or where ^{19}F NMR have not been reported (9 pages). Ordering information is given on any current masthead page.

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Reinvestigation of the Thermal Rearrangement of Alkenylidenecyclopropanes

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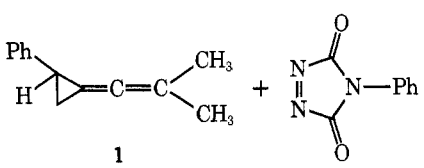
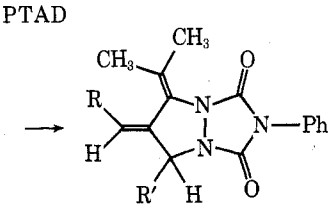
The thermal rearrangement of alkenylidenecyclopropanes has been reinvestigated. It is concluded that the thermal rearrangements occur via perpendicular trimethylenemethane-type diradicals and that the rearrangement is a typical methylenecyclopropane-type rearrangement. Contrary to the previously reported results, enantiomerization and diastereomerization of alkenylidenecyclopropanes is observed, and the activation enthalpies measured in this study are considerably lower than those reported. Whereas aryl-substituted alkenylidenecyclopropanes undergo thermal rearrangement under the more vigorous conditions required for cycloaddition with less reactive dienophiles, alkyl-substituted alkenylidenecyclopropanes rearrange much more slowly, allowing for reaction with the less reactive dienophiles.

In view of the tremendous synthetic utility of the [$_\pi$4 + $_\pi$2] cycloaddition reaction (i.e., the Diels–Alder reaction) for the construction of variously substituted cyclohexenes and the well-known tendency of the cyclopropyl moiety to mimic the carbon–carbon double bond in certain reactions, we embarked on a program designed to evaluate the synthetic utility of cycloaddition reactions of cyclopropane-containing compounds. Although methylenecyclopropanes[1] and vinylcyclopropanes[2] failed to undergo the desired cycloaddition reactions to form five- and seven-membered ring compounds even with the most reactive of the dienophiles, 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), alkenylidenecyclopropanes reacted rapidly at 0 °C in the desired manner to form five-membered ring compounds[3] with PTAD.

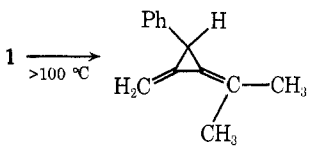


1 PTAD



R = Ph; R′ = H
R = H; R′ = Ph

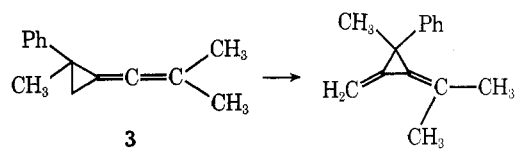
Attempts to react the easily prepared 1 with less reactive dienophiles (maleic anhydride and tetracyanoethylene) at higher temperatures (>100 °C) resulted in the thermal rearrangement of 1 to produce the bisalkylidenecyclopropane 2.[4]



2

Efforts were temporarily abandoned toward effecting cycloaddition reactions with less reactive dienophiles, and the intimate details of the cycloaddition of alkenylidenecyclopropanes with PTAD were investigated. Theoretical and spectroscopic studies[5] led to an understanding of the nature of the bonding in alkenylidenecyclopropanes and the bonding interactions in the transition state for concerted cycloaddition with PTAD, and the results of a kinetic study gave a value of $\Delta H^{\ddagger}$ for the cycloaddition of 1 with PTAD of 9.6 ± 1.5 kcal/mol.[6]

During the early stages of the later investigations the results of a study of the thermal rearrangement of arylsubstituted alkenylidenecyclopropanes were reported.[7] It was reported that the rearrangement of 3 to 4 occurred with a $\Delta H^{\ddagger}$ of 30.4



3 4

kcal/mol. Intuitively, this value seemed far too high in view of our observation that the rearrangement of 1 proceeded at a reasonable rate at ≳100 °C. Furthermore, the difference between the $\Delta H^{\ddagger}$ of 9.6 kcal/mol for cycloaddition of 1 with PTAD and >30.4 kcal/mol for rearrangement of 1 (the methyl group of 3 should lower the $\Delta H^{\ddagger}$ for rearrangement of 3 relative to 1) provides a rather large "thermodynamic window" between which we should have been able to find a dienophile capable of reacting with 1 with a $\Delta H^{\ddagger} > 9.6$ but <30.4 kcal/mol. Although the thermal rearrangement of the alkenylidenecyclopropanes appeared to be a typical methylenecyclopropane rearrangement, Sadler and Stewart[7] reported that diastereomerization of substituted alkenylidenecyclopropanes did not occur. In view of these unexpected reported aspects of the thermal rearrangements of alkenylidenecyclopropanes it was decided to reinvestigate the rearrangement reaction.

Results

The thermal rearrangements of 1, 3, 5, and 6 were carried out in sealed NMR tubes, the rates of rearrangement being