Research article

MRC

Received: 4 May 2015 Revised: 22 July 2015 Accepted: 30 July 2015 Published online in Wiley Online Library: 1 September 2015

(wileyonlinelibrary.com) DOI 10.1002/mrc.4327

Through-space ^{19}F–^{19}F spin–spin coupling in *ortho*-fluoro *Z*-azobenzene

Shiva K. Rastogi,[a] Robert A. Rogers,[a] Justin Shi,[a] Christopher T. Brown,[a] Cindy Salinas,[a] Katherine M. Martin,[a] Jacob Armitage,[a] Christopher Dorsey,[a] Gao Chun,[b] Peter Rinaldi[b] and William J. Brittain[a]*

We report through-space (TS) ^{19}F–^{19}F coupling for *ortho*-fluoro-substituted *Z*-azobenzenes. The magnitude of the TS-coupling constant ($^{TS}J_{FF}$) ranged from 2.2–5.9 Hz. Using empirical formulas reported in the literature, these coupling constants correspond to non-bonded F–F distances (d_{FF}) of 3.0–3.5 Å. These non-bonded distances are significantly smaller than those determined by X-ray crystallography or density functional theory, which argues that simple models of ^{19}F–^{19}F TS spin–spin coupling solely based d_{FF} are not applicable. ^{1}H, ^{13}C and ^{19}F data are reported for both the *E* and *Z* isomers of ten fluorinated azobenzenes. Density functional theory [B3YLP/6-311++G(d,p)] was used to calculate ^{19}F chemical shifts, and the calculated values deviated 0.3–10.0 ppm compared with experimental values. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: NMR; ^{19}F; ^{1}H; ^{13}C; azobenzene; through-space coupling; fluorinated azobenzene; *cis*-azoenzene

Introduction

Azobenzene (AB) is arguably the most studied organic chromophore in chemistry.[1] AB exists as two geometric isomers (Scheme 1) with the ***E*** conformation 50 kJ/mol more stable than the ***Z*** isomer. Excitation wavelengths for AB photoisomerization are dependent on the substituents, but generally, irradiation with 320–380 nm promotes ***E*** to ***Z*** isomerization, and the process is reversed with λ ~400–450-nm exposure or thermally by placing the sample in the dark.[2] ***Z***-AB adopts a bent conformation with the phenyl groups twisted 53° out of the plane of the azo group (this corresponds to the C_2C_1NN' dihedral angle in Table 1).[3] There are two pathways for isomerization: (i) in-plane inversion centered at one azo nitrogen and (ii) out-of-plane rotation about the N=N bond.[4] Depending on substituents and experimental conditions, either pathway can be operative. The isomerization occurs with little photodegradation; the increased dipole moment and smaller molecular cross section of ***Z***-AB have been exploited by using AB compounds as local environmental probes and stimuli in hybrid materials.[5] The focus of this report is the structure of the ***Z*** isomer and not the photoisomerization process. We have observed that through-space (TS) ^{19}F–^{19}F coupling in *ortho*-fluoro ***Z***-ABs, which we argue, provides an additional probe of conformation of ***Z***-AB in hybrid systems through the use of ^{19}F NMR.[6]

Results and discussion

Synthesis

Azobenzene compounds **1–8** (Scheme 1) were prepared via the diazonium salt intermediate[7] followed by iodomethane reaction with phenol. Compound **1** has been previously reported.[8] Compounds **9** and **11** were prepared from 2-nitrosobenzene derivatives and the corresponding aniline.[9] Belger *et al.*[10] reported the synthesis and photoisomerization of *p,p'*-disubstituted tetrafluoroazobenzene; we adopted their synthesis for compound **10**. Compounds **9** and **10** have been previously reported.[11] As prepared, the configuration of these compounds is principally the more stable ***E*** isomer, which can be converted to a mixture of ***Z*** and ***E*** within minutes using UV irradiation. The thermal ***Z*** to ***E*** isomerization is sufficiently slow so that isomer separation is possible by flash chromatography (R_f-***Z*** > R_f-***E*** for hydrocarbon mobile phase and silica absorbant).

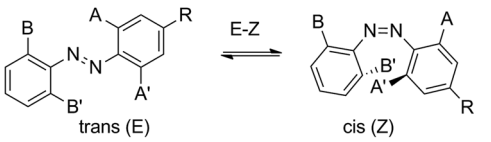
NMR studies

The geometric isomers of **1–11** exhibit distinct ^{1}H, ^{13}C and ^{19}F NMR spectra.[12] Table 2 lists the ^{19}F chemical shifts for **1–11**, and the data fall within a relatively narrow range chemical shift range. The fluorines on the methoxy-substituted ring are designated F_A. The ^{19}F chemical shifts are slightly solvent dependent with ~2-ppm shifts to higher frequency in toluene-d_8 compared with $CDCl_3$. Nuclei in the ***Z*** isomer are more shielded in the ^{1}H and ^{13}C NMR except for the ^{13}C shifts of the *ipso* ring. Steric deshielding has been previously reported for ABs[13] and related systems,[14] where there is close proximity of two carbon atoms. Based on the X-ray analysis of our systems, the *ipso* carbons are the only atoms having non-bonded distances less than the sum of the van der Waals radii. The X-ray distance between *ipso* carbons ranges from 2.71–3.12 Å

* *Correspondence to: William Brittain, Department of Chemistry and Biochemistry, Texas State University, 601 University Drive, San Marcos, TX 78666, United States. E-mail: wb20@txstate.edu*

a *Department of Chemistry and Biochemistry, Texas State University, 601 University Drive, San Marcos, TX, 78666, United States*

b *Department of Chemistry, The University of Akron, Akron, OH, 44325, United States*



1: A,A',B,B'=H, R=OMe
2: A=F, A',B,B'=H, R=OMe
3: A,A',B'=H, B=F, R=OMe
4: A,A'=H, B,B'=F, R=OMe
5: A,B=F, A',B'=H, R=OMe
6: A,A',B=F, B'=H, R=OMe
7: A,B,B'=F, A'=H, R=OMe
8: A,A',B,B'=F, R=OMe
9: A=F, A',B,B',R=H
10: A,B=F, A',B',R=H
11: A,A',B=F, B',R=H

Scheme 1. Cis–trans isomerization of *ortho*-substituted azobenzene.

Table 1. Calculated and X-ray structural parameters for ***Z*8**

	X-ray	DFT[a]	%Deviation
R(N,N')	1.257	1.243	1.1
R(N,C_1)	1.435	1.421	1.0
R(N'C_1')	1.418	1.426	0.6
C_2C_1NN'	58.55	51.80	11.5
$C_2'C_1'N'N$	58.45	56.00	4.2
$C_1NN'C_1'$	10.25	10.7	4.4
d_{FF}[b]	3.70	3.70	0.1
	4.72	4.93	7.9

R, bond length; Å, dihedral angles in degrees; DFT, density functional theory.
DFT method – B3YLP/6-311++G(d,p), gas phase.
[a]Values are for optimized ground-state geometry.
[b]Molecule exhibits two unique distances for intramolecular F–F.

Table 2. ^{19}F chemical shifts, ppm[a]

Compound	F_A	F_B	Compound	F_A	F_B
***E*2**	−121.68	—	***E*3**	—	−125.48
***Z*2**	−116.86	—	***Z*3**	—	−122.72
***E*4**	—	−122.68	***E*5**	−121.31	−125.30
***Z*4**	—	−120.41	***Z*5**	−118.10	−122.26
***E*6**	−117.59	−124.79	***E*7**	−121.27	−122.80
***Z*6**	−117.77	−122.69	***Z*7**	−119.62	−120.82
***E*8**	−117.63	−122.53	***E*9**	−121.70	—
***Z*8**	−117.77	−119.95	***Z*9**	−118.16	—
***E*10**	−124.57	—	***E*11**[b]	−121.73	−124.10
***Z*10**	−122.03	—	***Z*11**	−119.75	−122.89

[a]Experimental δ relative to $CFCl_3$ internal standard ($\delta = 0.00$).
[b]For compound **11**, F_A corresponds to ring with two Fs.

compared with a 3.40-Å sum of van der Waals radii. The ^{19}F chemical shifts for the ***Z*** isomer appear upfield relative to ***E*** isomer except for the F_A fluorines in ***Z*8**.

We evaluated density functional theory (DFT) as a tool to interpret chemical shift differences between the ***E*** and ***Z*** isomers. We used the 6-311++G(d,p)[15–18] and cc-pVTZ[19] basis sets and continuous set of gauge independent atomic orbitals (GIAO) for NMR calculations.[20,21] We note that application of DFT to conjugated, electron-rich systems is not without controversy. Klug and Burcl[22] published DFT results for AB photoisomerization, which were subsequently challenged by Meier on the basis that electron correlation was not fully included.[23] A comparison of calculated with experimental ^{19}F chemical shifts is provided in Table S1. The difference between calculated and observed ^{19}F chemical shifts ranged from 0.3 to 10.0 ppm. There was no correlation between calculated and experimental ^{19}F chemical shifts, and the difference between theory and experiment exceeds the observed chemical shift differences between ***Z*** and ***E*** isomers or the differences due to fluorine substitution patterns. DFT has shown more predictive value for ^{19}F chemical shifts in rigid systems.[17,19] Contreras[24] and Ono[25] reported similar multi-ppm differences between calculated and experimental ^{19}F chemical shifts in aliphatic fluorocarbons. Further refinement of DFT calculations is outside the scope of this paper.

Through-space coupling

For all ***E*** isomers, peaks appeared as singlets, and there was no evidence of TS coupling ($^{TS}J_{FF}$). For compounds with F on both rings (**5–8, 11**), TS coupling is observed in the ***Z*** isomer. The $^{19}F\{^1H\}$ spectra of 1-(2,6-difluoro-4-methoxyphenyl)-2-(2,6-difluorophenyl) diazene **(8)** and 1-(2,6-difluorophenyl)-2-(2-fluorophenyl)diazene **(11)** are shown in Fig. 1. ***Z*8** exhibits two triplets with $^{TS}J_{FF} = 4.6$ Hz, and ***Z*11** exhibits a doublet and triplet with $^{TS}J_{FF} = 5.9$ Hz. Splitting in ***Z*8** and ***Z*11** was not affected by solvent ($CDCl_3$, toluene-d_8 and CD_3CN). Normally, coupling constants are not strongly solvent dependent, although Mele *et al.*[26] reported a J_{FF} solvent dependence for fluoronucleosides, which was related to hydrogen-bonding ability of solvent. Intrinsic coupling constants are insensitive to solvent, and changes in observed values can be largely attributed to changes in conformational equilibria.[27] The ^{19}F homonuclear *J*-resolved NMR spectrum and ^{19}F–^{19}F COSY spectrum of ***Z*8** are shown in Fig. 2a and b and are consistent with F_A–F_B coupling.

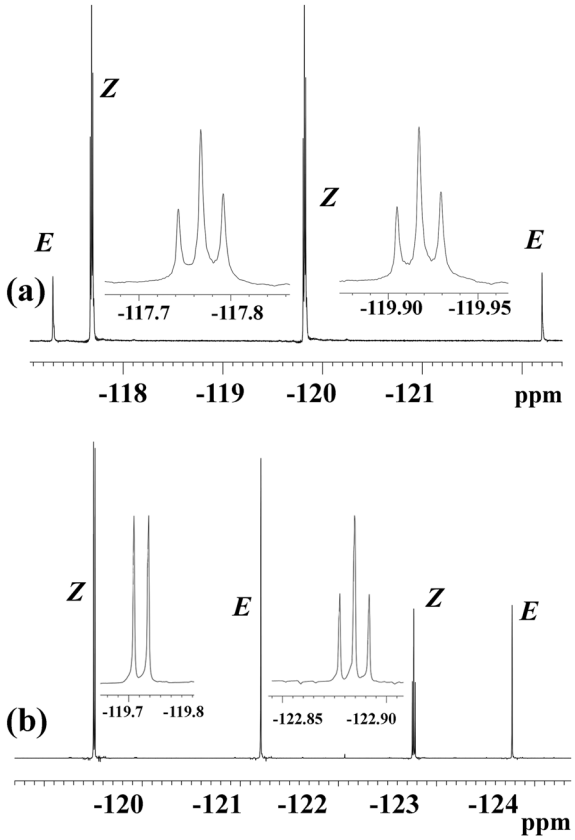


Figure 1. $^{19}F\{^1H\}$ NMR spectrum in $CDCl_3$ at 28 °C for ***E*8** and ***Z*8** (a) and ***E*11** and ***Z*11** (b).

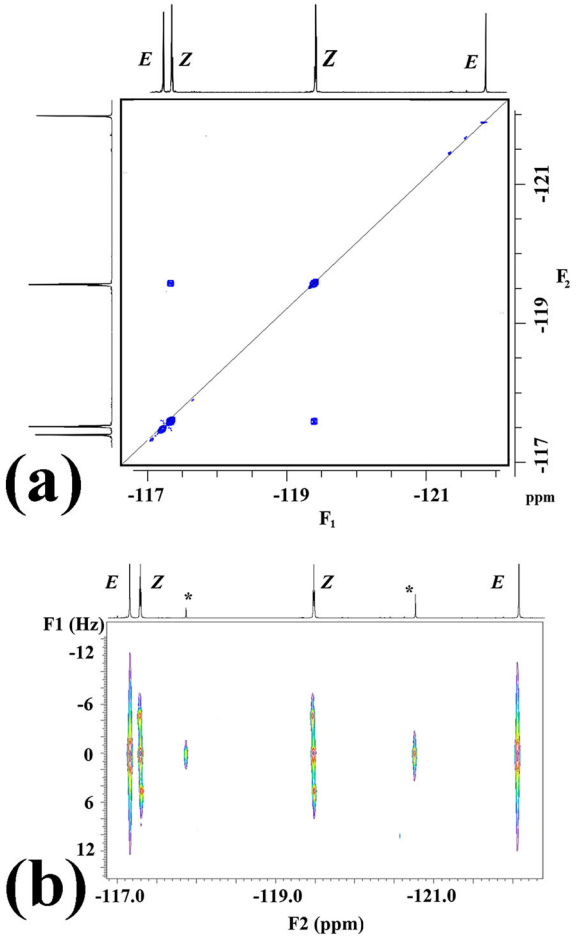


Figure 2. 2D NMR spectroscopy of ***E*8** and ***Z*8**: ^{19}F–^{19}F COSY (a) and 2D *J*-resolved (b); asterisk (*) denotes unidentified impurities.

Table 3 contains the experimentally observed TS coupling values, and they lie within a narrow range except for ***Z*5** whose lower value is a consequence of conformations having substantially different d_{FF}. Multiplicity followed the $(n+1)$ rule for TS ^{19}F–^{19}F coupling. No splitting was observed for ***E*** isomers, which argues that the coupling observed in the ***Z*** isomer is not a through-bond coupling; this statement is qualified by recognition that π-conjugation can produce larger contributions from the spin dipole term in Ramsey's[28] isotropic contributions to the spin–spin coupling constant (SSCC).[29] Based on the dihedral angle between the azo linkage and the phenyl groups, we estimate that only 38% effective p conjugation exists in ***Z*** isomers. This difference in conjugation may make comparison of ***E*** with ***Z*** TS coupling less valid.

Table 3. Comparison of through-space ($^{TS}J_{FF}$) *versus* non-bonded distance for ***Z***–AB compounds[a]

Compound	$^{7}J_{FF}$[d] (Hz)	d_{FF}, Å			
				Calculated from Exp. $^{TS}J_{FF}$	
		X-ray	DFT	Mallory[b]	Ernst[c]
***Z*5**	2.2 (d, d)	nd	4.30	3.20	3.65
***Z*6**	4.4 (d, t)	nd	4.82	3.06	3.44
***Z*7**	4.1 (t, d)	3.47	4.37	3.07	3.46
***Z*8**	4.6 (t, t)	4.22	4.31	3.03	3.40
***Z*11**	5.9 (d, t)	nd	4.10	2.99	3.35

DFT, density functional theory; nd, not done.
[a]Values are the average F–F distance.
[b]Mallory *et al.*[15]
[c]Ernst and Ibrom[33]
[d]Multiplicity given in parentheses where the first letter corresponds to peak at higher frequency.

For a non-bonded F–F distance (d_{FF}) ≤ 3.20 Å and for fluorines separated by four or more bonds, coupling is mediated primarily by 'TS' coupling.[15,30–32] For compounds **5,8–11**, the fluorines are separated by seven bonds, and most F–F distances exceed 3.20 Å. It is generally understood that 'TS' coupling occurs through a Fermi contact mechanism, but the key orbitals involved in TS coupling are still not known with confidence. In a study of thirteen 1,8-difluoronaphthalene compounds, Mallory *et al.*[15] reported an empirical equation for d_{FF} (pm) versus the SSCC: $J_{FF} = \left(1.703 \times 10^{7}\right)e^{-(4.96 d_{FF})}$. Similarly, Ernst and Ibrom[33] studied TS coupling in rigid cyclophanes and reported a similar exponential relationship – $^{TS}J_{FF} = (275000)e^{-(0.0321 d_{FF})}$. Mallory based his analysis on overlapping in-plane lp(π) orbitals on fluorine to explain the distance dependence of SSCC. Mallory's and Ernst's empirical formulas have two deficiencies: (i) The empirical correlation was based on organofluorine compounds with either rigid or structurally constrained systems, and 2) the relative orientation of C–F bonds is not included. The limitations of these empirical formulas are recognized.[34] Based on computations, Tuttle *et al.*[29] concluded that lp(σ) and lp(σ)–lp(σ) contributions are larger than lp(π) contributions and that TS coupling is maximized for a head-to-head orientation of F atoms. Contreras *et al.*[35] reported that the Fermi contact term is the largest contributor to J_{FF} SSCCs; the second largest is the paramagnetic spin–orbit term. The paramagnetic spin–orbit term shows an unsymmetric second rank tensor characterized by the 'geometric effect'. The literature does not have sufficient guidance on proper inclusion of the 'geometric effect' in our data analysis. Because we have observed a range of C-F–F-C dihedral angles, we expect the geometry effect between fluorines to be important, and we regard our conclusions as qualitative.

Structural analysis

Assessment of the SSCC–d_{FF} empirical relationships requires independent determination of d_{FF}. We have measured this intramolecular distance by both X-ray crystallography and DFT. In solution-state studies of non-bonded interactions like TS coupling, DFT data are preferred because X-ray interatomic distances can be distorted by crystal packing forces.[6,33] Our X-ray data are limited to three ***Z*** structures (***Z*7–9**) because ***Z*** isomers typically form oils and suitable X-ray crystals were difficult to obtain. Figure 3 depicts the crystal structures of ***Z*7** and ***Z*8.** The parent ***Z***-AB (***Z***-1,2-phenyldiazene) is

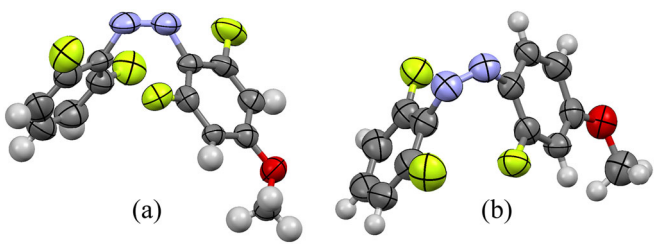


Figure 3. X-ray structures of ***Z*8** (a) and ***Z*7** (b).

distorted from planarity with a C-N=N-C dihedral angle of 8° and phenyl ring torsion of 53.3.[3] The crystal structures of ***Z*8** and ***Z*7** show similar distortions. The data in Tables 1, S1 and S2 show that compared with X-ray, DFT underestimates the torsion angle of the aromatic ring to azo group (C_2-C_1-N=N) and d_{FF}. The unsubstituted phenyl ring exhibits a higher torsion angle, which is due to *para*-methoxy rather than *ortho*-fluorine substitution. The DFT-minimized structure of ***Z***-1-(4-methoxyphenyl)-2-phenyldiazene exhibits a 43° torsion for the substituted aromatic ring. Introduction of fluorine into the *ortho* positions does not significantly alter twist angles, which is consistent with the work by Mazzanti *et al.*[36] on biphenyl rotational barriers that indicated that the steric size of fluorine is similar to hydrogen.

Conclusions

We have observed TS ^{19}F–^{19}F coupling in ***Z***-AB and supported our TS assignment using ^{19}F–^{19}F COSY and 2D *J*-resolved NMR spectroscopy. The empirical equations of Mallory and Ernst predict much shorter F–F distances when applied to our experimental values of TS coupling. DFT and X-ray structures indicate F–F distances (d_{FF}) greater than 3.47 Å, which would not be expected to show TS coupling. We did not include the geometrical relationship between interacting C–F groups and are currently developing more inclusive formulas for d_{FF} versus SSCC. Cormanich *et al.*[37] found that the calculated C-F–F-C distances are very sensitive to the choice of DFT basis set and this is also another current area of investigation. Attempts to use DFT for NMR calculations were unsuccessful with the deviation between theory and experiment in excess of changes due to geometrical isomerism or fluorine substitution pattern.

Experimental

General information

Unless otherwise noted, all reagents were obtained from commercial sources and used without purification. Flash chromatography used Agela 60-Å gel, and TLC was performed using EMD Millipore (Billerica, MA, USA) silica plates with fluorescent indicator. Absorption measurements were performed using either a Cary 100 Bio UV–vis spectrometer or an Ocean Optics (Dunedin, FL, USA) component system with a HR2000+ detector, qpod^{TM} sample holder, DH 2000 source and Spectra Suite software for data collection. Solutions were degassed via three freeze–pump–thaw cycles. Photochemical kinetic experiments used Oriel (Newport Corporation, Irvine, CA, USA) 66901 50–200-W Research Arc Lamp; the output was cooled with a water filter and passed through a bandpass filter (350-nm center, 70-nm FWHM). X-ray crystallography was performed on a Rigaku (Rigaku Americas, The Woodlands, TX, USA) SCX-Mini Single Crystal X-ray Diffractometer.[38]

Routine NMR spectra were obtained using a Bruker (Billerica, MA, USA) Advance III 400 spectrometer. ^1H and ^{13}C NMR shifts are reported relative to TMS, and ^{19}F shifts are relative to $CFCl_3$ (0.00 ppm). All ^{19}F spectra were collected with broadband proton decoupling.

^{19}F homonuclear 2D *J* NMR spectra were collected from a Varian (Palo Alto, CA, USA) Direct Drive 500-Mhz spectrometer equipped with five broad band rf channels and a 5-mm $^1H/^{19}F/^{13}C$ triple resonance pulse field gradient probe. This probe was made special for detecting fluoro-materials, because there are no fluorine-containing materials near the coil in order to avoid the interference from the background fluorine signals that usually exist in the standard probes. The high-frequency channel on this probe is doubly tuned to ^1H and ^{19}F to produce short 90° pulse widths needed to excite large fluorine spectral windows. A duplexer with low insertion loss provides the capability of combining the signals from the ^1H and ^{19}F rf channels and directing them to the dual-tuned $^1H/^{19}F$ high-frequency channel of the probe. The returning ^1H and ^{19}F signals from the probe can be separated by this duplexer again and the desired signal (^1H or ^{19}F) directed to the receiver. The sample was prepared by dissolving approximately 10 mg of material in a solvent mixture of $CDCl_3/CH_2Cl_2/CCl_4$ (27/60/13) (v/v/v) with a trace of $CFCl_3$ added as a chemical shift reference. The ^{19}F 1D NMR spectra were collected with a 5.2-kHz spectra window, 1.0-s relaxation delays, 2.0-s acquisition time and 3.5-μs (30°) pulse width; 64 transients were averaged with continuous ^1H decoupling using WALTZ-16 modulation ($\gamma_H B_H/2\pi = 2.7$ kHz). The data were zero filled to 256 k and exponentially weighted with a line broadening of 0.5 Hz before FT.

Computational details

Density functional theory[39] calculations were performed with the 6-311++G(d,p) basis set and the restricted B3YLP functional and cc-pVTZ basis set implemented in Gaussian 09.[40] Geometry optimizations, frequency calculations and NMR calculations were carried without solvent. Continuous set of gauge transformations[20,21] method was used for NMR calculations and isotropic values converted to ppm using the equation: ^{19}F δ: $\delta_{calc} = (-0.914^* \delta_{isotropic}) + 142.63$. T. Lectka, private communication.

General synthesis

Synthesis of **1–8** followed the procedure of Siewierski *et al.*[6] where the diazonium salt was formed under acidic conditions and reacted with a basic aqueous solution of the phenol. The crude product was then treated with 2-equivalent iodomethane in acetonitrile with 2-equivalent K_2CO_3 to afford crude product. Compounds **9** and **11** synthesis followed the procedure of Dong *et al.*,[9] and synthesis of **10** followed the report of Belger *et al.*[10] All compounds were purified by flash chromatography using mixtures of toluene and hexane. ***Z*** and ***E*** isomers were assigned by comparison of spectra for ***E*** versus ***E*/*Z*** mixture. For the description of general synthesis methods, see the study of Merino.[41] Spectra are provided in Supplementary Information.

1-(2-Fluoro-4-methoxyphenyl)-2-phenyldiazene ***E*2**. ^1H NMR (400.13 MHz, $CDCl_3$, δ) 3.87 (s, 3H, OCH_3), 6.77 (m, 1H), 6.79 (m, 1H), 7.5 (m, 3H), 7.83 (m, 1H), 7.95 (m, 2H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.2 (Me_3O), 102.5 (C3), 111.0 (C5), 1181.8 (C6), 123.1 (C8, 12), 129.4 (C9, C11), 131.1 (C10), 135.3 (C1), 161.9 (C2), 153.4 (C7), 163.7 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −121.68. UV (hexane) λ_{max}, nm (ε): 347 (19 000). ***Z*2**: ^1H NMR (400.13 MHz, $CDCl_3$, δ) 3.75 (s, 3H, OCH_3), 6.49 (m, 1H), 6.52 (m, 1H), 6.77 (m, 1H), 6.90 (m, 2H), 7.18 (m, 1H), 7.27 (m, 2H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 55.8 (Me_3O), 102.3 (C3), 110.1 (C5), 122.5 (C6), 123.1 (C8, 12), 128.1 (C9, C11), 129.1 (C10), 135.5 (C1), 152.4 (C2), 154.5 (C7), 161.1 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −116.86.

1-(2-Fluorophenyl)-2-(4-methoxyphenyl)diazene ***E*3**. ^1H NMR (400.13 MHz, $CDCl_3$, δ) 3.89 (s, 3H, OCH_3), 7.02 (m, 2H), 7.22 (m, 2H), 7.40 (m, 1H), 7.76 (m, 1H), 7.97 (m, 2H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 55.9 (Me_3O), 114.6 (C2, C6), 117.2 (C9), 118.1 (C12), 124.5 (C11),

125.5 (C2, C6), 132.0 (C10), 141.1 (C7), 147.6 (C1), 160.1 (C8), 162.7 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −125.48. UV (hexane) λ_{max}, nm (ε): 336 (16 000). ***Z2***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.77 (s, 3H, OCH_3), 6.77 (m, 2H), 6.96 (m, 2H), 6.98 (m, 2H), 7.09 (m, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 55.7 (Me_3O), 114.0 (C3, C5), 116.8 (C9), 122.2 (C12), 123.5 (C2, C6), 124.9 (C11), 128.7 (C10), 142.4 (C7), 147.4 (C1), 150.1 (C8), 160.0 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −122.72.

1-(2,6-Difluorophenyl)-2-(4-methoxyphenyl)diazene ***E4***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3. 90 (s, 3H, OCH_3), 7.01 (d, 4H), 7.27 (m, 1H), 7.94 (d, 2H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.0 (Me_3O), 112.7 (C9, C11), 114.6 (C3, C5), 125.4 (C2, C6), 129.7 (C10), 131.9 (C7), 148.1 (C1), 156.0 (C8, C12), 163.1 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −122.68. UV (hexane) λ_{max}, nm (ε): 311 (22 000). ***Z4***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.77 (s, 3H, OCH_3), 6.80 (d, 4H), 6.90 (d, 2H), 7.13 (m, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 55.7 (Me_3O), 112.3 (C9, C11), 114.1 (C3, C5), 122.5 (C2, C6), 128.4 (C10), 131.8 (C7), 148.3 (C1), 151.7 (C8, C12), 160.5 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −120.41.

1-(2-Fluoro-4-methoxyphenyl)-2-(2-fluorophenyl)diazene ***E5***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.88 (s, 3H, OCH_3), 6.76 (m, 2H), 7.22 (m, 2H), 7.42 (m, 1H), 7.77 (t, 1H), 7.84 (t, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.0 (Me_3O), 102.3 (C3), 111.3 (C4), 117.3 (C9, C11), 118.6 (C6), 119.2 (C12), 132.5 (C10), 132.5 (C10), 135.7 (C7), 141.3 (C1), 160.4 (C2), 162.2 (C8), 164.2 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −121.31, −125.30. UV (hexane) λ_{max}, nm (ε): 335 (14 000). ***Z5***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.77 (s, 3H, OCH_3), 6.53 (2H), 6.80 (1H), 6.98 (2H), 7.08 (1H), 7.15 (1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.0 (Me_3O), 102.4 (C3), 110.5 (C5), 116.7 (C9), 121.8 (C11), 121.9 (C12), 122.7 (C6), 129.4 (C10), 135.8 (C7), 142.6 (C1), 150.5 (C8), 152.8 (C2), 161.1 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −118.10, −122.26.

1-(2,6-Difluoro-4-methoxyphenyl)-2-(2-fluorophenyl)diazene ***E6***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.89 (s, 3H, OCH_3), 6.62 (d, 2H), 7.27 (m, 1H), 7.47 (m, 2H), 7.72 (t, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.4 (Me_3O), 99.2 (C3, C5), 117.3 (C9), 117.9 (C11), 124.6 (C12), 126.0 (C1), 134.0 (C10), 141.9 (C7), 158.0 (C2, C6), 160.2 (C8), 162.4 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −117.59, −124.79. UV (hexane) λ_{max}, nm (ε): 335 (14 000). ***Z6***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.77 (s, 3H, OCH_3), 6.36 (d, 2H), 7.01 (m, 2H), 7.10 (t, 1H), 7.20 (m, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 54.2 (Me_3O), 98.5 (C3, C5), 116.8 (C9), 117.6 (C11), 124.5 (C12), 125.6 (C1), 130.0 (C10), 143.1 (C7), 152.6 (C2, C6), 151.0 (C8), 160.9 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −117.77, −122.69.

1-(2,6-Difluorophenyl)-2-(2-fluoro-4-methoxyphenyl)diazene ***E7***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.89 (s, 3H, OCH_3), 6.75 (m, 1H), 6.77 (m, 1H), 7.02 (m, 2H), 7.29 (t, 1H), 7.78 (t, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.3 (Me_3O), 102.2 (C3), 111.4 (C5), 112.7 (C9, C11), 118.7 (C6), 131.9 (C20), 132.2 (C7), 136.1 (C1), 156.2 (C8, C12), 162.3 (C2), 164.7 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −121.27, −122.80. UV (hexane) λ_{max}, nm (ε): 335 (14 000). ***Z7***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.77 (s, 3H, OCH_3), 6.56 (m, 2H), 6.85 (m, 2H), 6.90 (m, 1H), 7.20 (m, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.1 (Me_3O), 102.5 (C3), 110.2 (C5), 112.3 (C9, C11), 122.6 (C6), 1232.1 (C10), 132.1 (C7), 136.45 (C1), 151.7 (C8, C12), 153.2 (C2), 161.4 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −119.62, −120.82.

1-(2,6-Difluoro-4-methoxyphenyl)-2-(2,6-difluorophenyl)diazene ***E8***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.89 (s, 3H, OCH_3), 6.70 (d, 2H), 7.13 (t, 2H), 7.41 (m, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.5 (Me_3O), 99.2 (C3, C5), 112.8 (C9, C11), 126.4 (C1), 130.8 (C10), 155.8 (C2, C6), 157.8 (C8, C12), 162.9 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −117.63, −122.53. UV (hexane) λ_{max}, nm (ε): 331 (14000). ***Z8***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 3.75 (s, 3H, OCH_3), 6.48 (d, 2H), 6.96 (t, 2H), 7.29 (m, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 56.3 (Me_3O), 98.7 (C3, C5), 112.4 (C9, C11), 126.3 (C1), 129.8 (C10), 132.6 (C7), 152.2 (C8, C12), 153.3 (C2, C6), 161.4 (C4). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −117.77, −119.95.

1-(2-Fluorophenyl)-2-phenyldiazene ***E9***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 7.23 (m, H5), 7.29 (m, H3), 7.45 (m, H4), 7.53 (m, H9, H11), 7.79 (m, H6), 7.98 (m, H8, H12). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 117.3 (C3), 118.0 (C6), 123.4 (C8, C12), 124.5 (C5), 129.3 (C9, C11), 131.7 (C10), 132.7 (C4), 140.9 (C1), 153.0 (C7), 161.5 (C2). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −121.70. ***Z9***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 6.88 (m, H5), 6.90 (m, H3), 6.95 (m, H9, H11), 7.04 (m, H6), 7.11 (m, H4), 7.24 (m, H10), 7.27 (m, H8, H12). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 116.5 (C3), 120.1 (C9, C11), 122.0 (C5), 124.5 (C6), 128.3 (C10), 128.9 (C8, C12), 129.0 (C4), 142.0 (C1), 149.1 (C7), 152.9 (C2). ^{19}F (376.50 MHz, $CDCl_3$, δ) −118.16.

1,2-bis(2-Fluorophenyl)diazene ***E10***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 7.05 (t, H3, H5), 7.31 (m, H10), 7.54 (m, H4, H9, H11), 7.95 (m, H8, H12). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 112.8 (C3, C5), 123.3 (C8, C12), 129.4 (C9, C11), 130.1 (C10), 131.7 (C1), 132.2 (C4), 153.5 (C7), 156.0 (C2, C6). ^{19}F NMR (376.50 MHz, $CDCl_3$, −124.57. ***Z10***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 6.78 (m, H3, H5), 6.92 (d, H8, H12), 7.08 (m, H4), 7.20 (m, H10), 7.25 (m, H9, H11). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 112.0 (C3, C5), 119.0 (C8, C12), 128.8 (C4), 128.9 (C10), 131.6 (C1), 151.1 (C2, C6), 155.2 (C7). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −122.03.

1-(2,6-Difluorophenyl)-2-(2-fluorophenyl)diazene ***E11***. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 7.19 (t, 2H), 7.40 (m, 2H), 7.51 (m, 1H), 7.64 (m, 1H), 7.71 (m, 1H). ^{13}C NMR (100.61 MHz, $CDCl_3$, δ) 113.2 (C3, C5), 113.9 (C9), 121.6 (C11, C12), 125.8 (C1), 132.9 (C4), 142.0 (C7), 156.6 (C2, C6), 161.0 (C8). ^{19}F NMR (376.50 MHz, $CDCl_3$, δ) −121.73, −124.10. ***Z11***: ^{1}H NMR (400.13 MHz, $CDCl_3$, δ) 6.97 (t, 2H), 7.15 (m, 2H), 7.31 (m, 3H). ^{13}C (100.61 MHz, $CDCl_3$, δ) 113.1 (C3, C5), 113.7 (C9), 121.6 (C11, C12), 125.6 (C1), 131.7 (C4), 132.9 (C10), 143.4 (C7), 152.0 (C2, C6), 152.2 (C8). ^{19}F (376.50 MHz, $CDCl_3$, δ) −119.75, −122.89.

Acknowledgements

W. J. B. thanks T. Lectka for the helpful advice and the National Science Foundation (PREM Center for Interfaces, DMR-1205670) and the ACS Petroleum Research Fund (51997UR7) for the financial support of this research. The authors also acknowledge the support of the National Science Foundation for X-ray and NMR instrumentation (CR1IF:MU-0946998 and MRI-0821254) and the Welch Foundation (AI-0045).

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