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Organic Glass-Forming Materials: 1,3,5-Tris(naphthyl)benzene Derivatives

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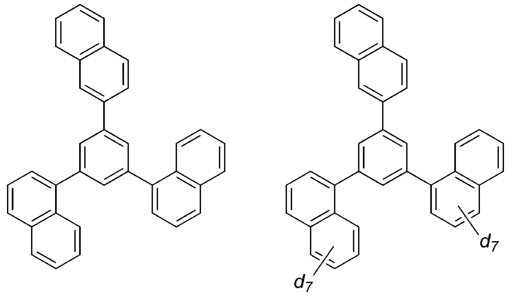
Received August 31, 2007



The organic glass-forming materials 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**) and its partially deuterated analogue, 1,3-bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (**2**-d_{14}), have been synthesized on a gram scale using Suzuki coupling reactions. Detailed spectroscopic studies afford complete NMR assignments (^{1}H, ^{2}H, ^{13}C) for both compounds. Modest energy barriers for the interconversion of atropisomers (ca. 15 kcal/mol) result in a propensity for these materials to form supercooled liquids and glasses, rather than undergoing crystallization. The preparation of these materials enables detailed studies of physical properties of organic glasses and molecular diffusion in condensed phases.

Introduction

Organic glass-forming materials find varied application in modern science and technology. Organic polymers with high glass transition temperatures are used as dielectric insulating layers in microelectronic devices.[1,2] Amorphous organic materials play an important role as electroluminescent materials in optoelectronic device applications.[3,4] Considerable attention is focused on amorphous (glassy) formulations of pharmaceuticals.[5,6] With respect to basic scientific issues, fundamental questions persist concerning the physical properties of glassy materials and the nature of the glass transition.[7−10]

The relationship between the molecular structure of an organic material and the propensity for forming a glassy phase is not well established, although a commonly encountered structural motif involves a biaryl linkage. Two such systems of longstanding interest in the field of glassy materials are *o*-terphenyl and 1,3,5-tris(naphthyl)benzene.[3,4,11] Qualitatively, a moderate energy barrier to interconversion of atropisomers enhances the likelihood that these compounds will form an amorphous glass, rather than a crystalline solid, upon cooling from the liquid phase. Several years ago, we described the

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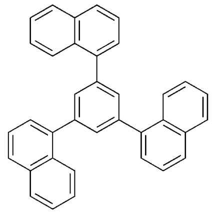

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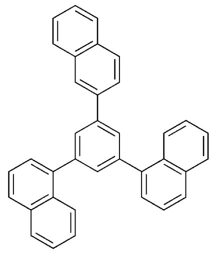

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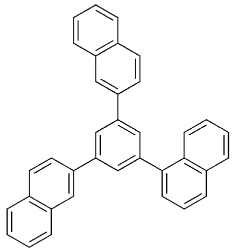

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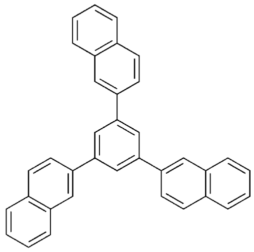

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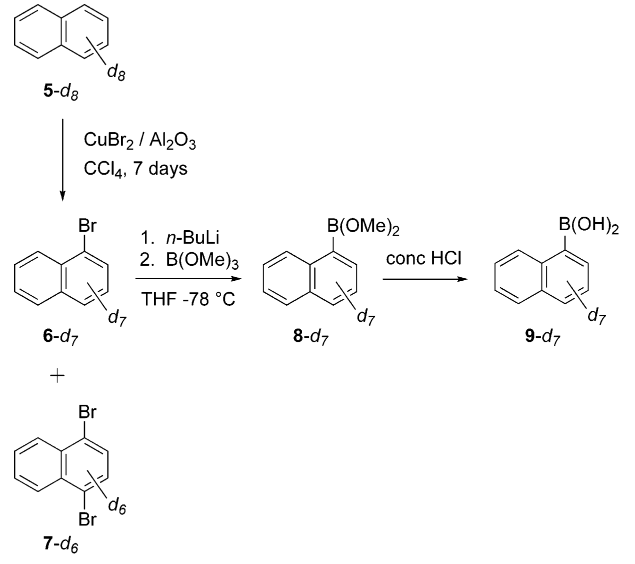
preparation of a series of molecular glass-forming materials **1**−**4** based on the 1,3,5-tris(naphthyl)benzene motif.[12] This study revealed misconceptions and misassignments in earlier work in the field, establishing that (i) the atropisomers of 1,3,5-tris-(1-naphthyl)benzene (**1**) are not separable, but interconvert rapidly on the NMR time scale in solution at room temperature, and (ii) the structure of material that had been widely studied in the field was 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**), not 1,3,5-tris(1-naphthyl)benzene (**1**). The study also provided a rare instance in which changes in bulk physical properties (i.e., glass transition temperature) could be rationalized in terms of changes in molecular structure.[12]

The availability of the 1,3-bis(1-naphthyl)-5-(2-naphthyl)-benzene (**2**) made possible a series of important investigations concerning diffusion in glasses and the physical properties of glassy materials.[13−15] Crucial experiments in these investigations relied on the preparation of partially deuterated substrates.[13−15] In the current manuscript, we describe the preparation and detailed spectroscopic characterization of 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**) and its deuterated analogue, 1,3-bis-(1-naphthyl-d_7)-5-(2-naphthyl)benzene (**2**-d_{14}).

Synthesis

Experimental measurements of self-diffusion in glass-forming materials rely on concentration profiling methods such as forward recoil elastic spectrometry (FRES),[13] neutron reflectivity,[14] secondary-ion mass spectrometry (SIMS), and thermally programmed desorption. These techniques, which require the use of both protio and deuterio samples, rely on the ability to detect differences in either mass or scattering properties between the isotopomers. It became necessary, therefore, to prepare a heavily deuterated 1,3,5-tris(naphthyl)benzene isotopomer. The position of deuterium substitution is not a crucial issue; the degree of deuterium substitution is. In our initial approach, we attempted to introduce deuterium in 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**) by catalytic H/D exchange. These catalytic methods have been effective in the preparation of perdeuterated isotopomers of simple aromatic hydrocarbons.[16,17] With our substrate, however, mild reaction conditions failed to yield (appreciable) H/D exchange, while more vigorous conditions led to sample decomposition.

SCHEME 1



Our subsequent approach for the preparation of a deuterated isotopomer of **2** relied upon chemical synthesis from commercially available deuterated starting materials. The desire to achieve the highest possible level of deuterium incorporation was tempered by the synthetic challenges posed by the preparation of perdeuterated derivatives of both 1- and 2-substituted naphthalene. Given the commercial availability of naphthalene-d_8 and the fact that electrophilic aromatic substitution of naphthalene affords a significant preponderance of the 1-substituted product, we established 1,3-bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (**2**-d_{14}) as our synthetic target. It seemed prudent to introduce the deuterated fragments at a late stage of the synthesis. The earlier synthesis of 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**) involved introduction of the 1-naphthyl substituents, first, followed by introduction of the 2-naphthyl substituent.[12] In the current synthesis, reversing the order of these coupling reactions showed no significant effect on the overall chemical yield (see below).

The synthesis of the requisite 1-naphthylboronic acid-d_7 (**9**-d_7) was achieved in two steps (Scheme 1). Selective bromination of naphthalene-d_8 (**5**-d_8) using a slurry of copper(II) bromide on alumina in CCl$_4$ (26−29 °C, 7 days) yielded 1-bromonaphthalene-d_7 (**6**-d_7) with good selectivity and chemical yield (ca. 75%).[18] The optimum temperature was found to be 26−29 °C; at temperatures above 30 °C, formation of 1,4-dibromonaphthalene-d_6 (**7**-d_6) becomes problematic. Conversion of 1-bromonaphthalene-d_7 (**6**-d_7) to 1-naphthylboronic acid-d_7 (**8**-d_7) was effected by metal−halogen exchange using n-BuLi, followed

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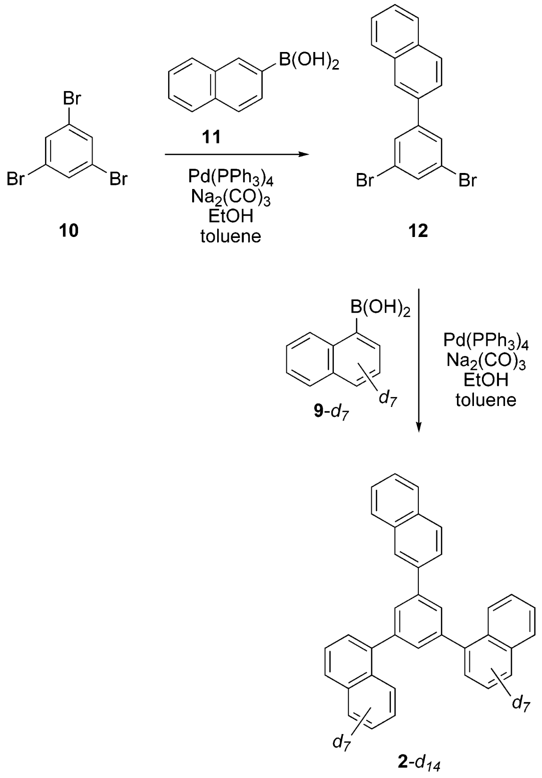
SCHEME 2



by treatment with trimethylborate. The resulting dimethoxy-1-naphthylborane-d_7 (**8**-d_7) was hydrolyzed in concentrated HCl to afford the desired 1-naphthylboronic acid-d_7 (**9**-d_7) in ca. 65% yield.[12]

The target molecule, 1,3-bis(1-naphthyl-d_7)-5-(2-naphthyl)-benzene (**2**-d_{14}), was assembled using sequential Suzuki coupling reactions (Scheme 2). Reaction of 1,3,5-tribromobenzene (**10**) with 2-naphthylboronic acid (**11**; 1.0 equiv) afforded 1,3-dibromo-5-(2-naphthyl)benzene (**12**) in 65% yield.[12] Subsequent reaction of 1,3-dibromo-5-(2-naphthyl)benzene (**12**) with 1-naphthylboronic acid-d_7 (**9**-d_7; 2.4 equiv) afforded 1,3-bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (**2**-d_{14}) in 53% yield.

NMR Spectroscopy

An unrealized goal in the field of glassy materials involves the development of physical models that correlate molecular structure and conformational dynamics with bulk physical properties. We sought to obtain detailed NMR spectroscopic data for compounds **2** and **2**-d_{14}, with the expectation that these data may provide a valuable context for interpreting experiments involving bulk physical properties of **2**. Of additional interest, compounds **2** and **2**-d_{14} present challenging applications for state-of-the-art NMR techniques. An aromatic hydrocarbon with no other functional groups, tris(naphthyl)benzene **2**, exhibits very small chemical shift dispersion in the ^{1}H and ^{13}C NMR spectra. All 24 protons of **2** fall within a chemical shift range of only 0.7 ppm, and these resonances have substantial overlap even at high magnetic field strengths. All 36 carbon atoms fall within 16 ppm. Only through combined studies of the protio and deuterio isotopomers (**2** and **2**-d_{14}), utilizing a variety of 2D NMR techniques, were NMR assignments achieved.

Variable-temperature ^{13}C NMR spectra establish that conformational interconversion among atropisomers of 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**) is rapid on the NMR time scale at room temperature.[12,19] Rotation about the aryl-1-naphthyl bond, which has a measured barrier of ca. 12 kcal/mol, is frozen out at 193 K. Rotation about the aryl-2-naphthyl bond, which has a computed barrier of 2 kcal/mol, has not been frozen out. All spectra in the current investigation were obtained at room temperature, which is within the limit of fast exchange for **2** and **2**-d_{14}.

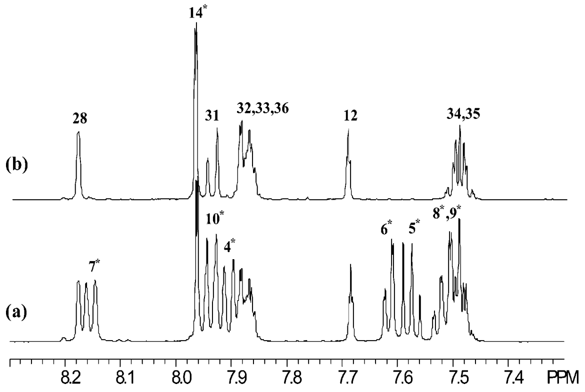
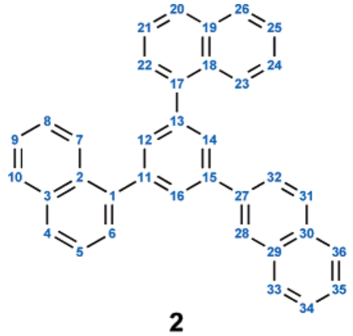


FIGURE 1. ^{1}H NMR spectra (500 MHz): (a) compound **2**; (b) compound **2**-d_{14}. * = two positions are equivalent through rapid dynamic averaging.



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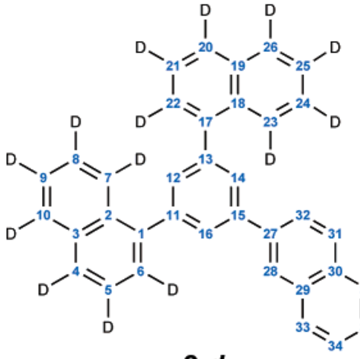

2-d_{14}

^{1}H NMR spectra of **2** and **2**-d_{14}, acquired at 500 MHz, are shown in Figure 1. (Spectra obtained at 600 MHz did not provide directly useful improvements in resolution.) The ^{1}H NMR assignments for **2** are listed in Table 1, which also includes a listing of cross-peaks observed in the gDQ-COSY spectrum (Figure S1, Supporting Information). The ^{1}H NMR assignments for **2**-d_{14} are also available (Table S1, Supporting

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TABLE 1. **^{1}H NMR Assignments for 1,3-Bis(1-naphthyl)-5-(2-naphthyl)benzene (2)**

proton	δ (ppm)	intg.[a]	mult	J (Hz)[b]	COSY[c]
H-28	8.176	1.0	d	1.1	32, 31(w)
H-7, H-23	8.153	1.9	d	8.0	8, 9, 4(w), 10(w)
H-14, H-16	7.962	2.0	d	1.5	12
H-31, H-10, H-26	7.936	3.0	d, d[d]	8.2	32, 8
H-4, H-20	7.904	2.1	dt	8.1, 0.9	6, 5
H-32	7.880	1.2	m[e]	1.7	28, 31
H-33, H-36	7.865	1.9	m[e]	2.1	34, 35
H-12	7.685	0.9	t	1.5	14, 16
H-6, H-22	7.616	1.9	dd	7.0, 1.2	5, 4(w)
H-5, H-21	7.574	1.9	t	7.5	4, 6
H-8, H-24, H-9, H-25	7.520[f]	3.5	ddd	6.9, 6.8, 1.2	10, 34(w)
H-34, H-35	7.488[f]	2.5	m	second order	32, 7

[a] Standard integral value (Table 2 lists intensities). [b] J-coupling values are provided only for resolved couplings. [c] COSY correlations are given from gDQ-COSY spectra; weak cross-peaks are followed by (w); the (near-) equivalent protons (e.g., 22 for 6) are not listed. [d] Two separate, partially resolved doublets are observed. [e] Resonances for H-32, H-33, and H-36 are overlapping and not resolved. [f] Resonances for H-8, H-9, and H-34, H-35 have estimated centers-of-mass as indicated by δ but are severely overlapping.

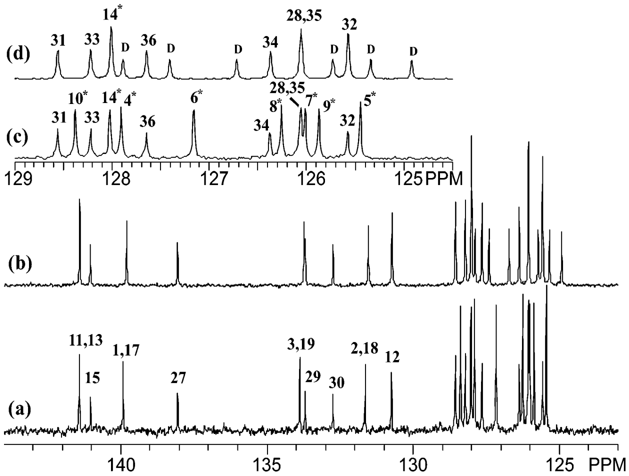

FIGURE 2. ^{13}C NMR spectra (125 MHz): (a) ^{13}C{^{1}H} spectrum of **2**; (b) ^{13}C{^{1}H,^{2}H} spectrum of **2**-d_{14}; (c) expansion of (a); (d) expansion of (b). * = two positions are equivalent through rapid dynamic averaging.

Information). Many ^{1}H assignments for **2** and **2**-d_{14} can be made on the basis of homonuclear J-couplings and ^{1}H chemical shifts. Protons 28, 14 and 16, 12, and 34 and 35 are straightforwardly assigned using the ^{1}H 1-D spectrum and the gDQ-COSY spectrum of **2**-d_{14}. Hetero-correlation data are required, however, to make complete ^{1}H assignments for each compound.

^{13}C NMR spectra of **2** and **2**-d_{14} are shown in Figure 2. The spectrum for **2** was acquired in the normal manner, with high-power proton decoupling applied throughout the experiment (^{13}C{^{1}H} spectrum). The spectrum for the partially deuterated compound **2**-d_{14} required the use of a technique that enabled decoupling of both ^{1}H and ^{2}H in the ^{13}C NMR spectrum (^{13}C{^{1}H,^{2}H} spectrum). A three-channel spectrometer, in which the ^{2}H lock channel of the probe was used for high-power deuterium decoupling, was used to acquire the ^{13}C{^{1}H,^{2}H} NMR spectrum in which all carbon resonances appear as singlets (Figure 2a). (Details concerning triple resonance ^{1}H/^{13}C/^{2}H experiments are available as Supporting Information.) Carbons C-28 and C-35 (or C-34) exhibit accidental overlap and are not resolved in the ^{13}C 1-D spectra. Carbons of **2**-d_{14} bearing ^{2}H are easily identified by comparing the ^{13}C{^{1}H,^{2}H} and ^{13}C{^{1}H} spectra (Figure 3). The ^{13}C{^{1}H,^{2}H} spectrum shows *all* carbons as singlets, while the ^{13}C{^{1}H} spectrum is depleted of carbons bearing ^{2}H. (Carbons bearing ^{2}H are nearly unobservable in the ^{13}C{^{1}H} spectrum because one-bond ^{13}C−^{2}H couplings split these signals into 1:1:1 triplets and longer-range ^{13}C−^{2}H couplings broaden those lines nearly into the noise.) Only six of the seven expected ^{13}C nuclei bearing ^{2}H are readily apparent, however (Figure 3d). An additional experiment was required to resolve this discrepancy. A ^{13}C{^{2}H} INEPT spectrum,[20] which detects *only* those ^{13}C nuclei bonded to ^{2}H, reveals all seven of the carbons bearing ^{2}H in **2**-d_{14} (Figure 4b,d). One carbon resonance bearing ^{2}H was overlapped with C-32 in the ^{13}C{^{1}H,^{2}H} spectrum (Figure 4c,d). Carbon assignments are tenuous, however, when only ^{13}C chemical shifts are available. Heteronuclear 2-D data are required to assign most of the carbon nuclei in each compound.

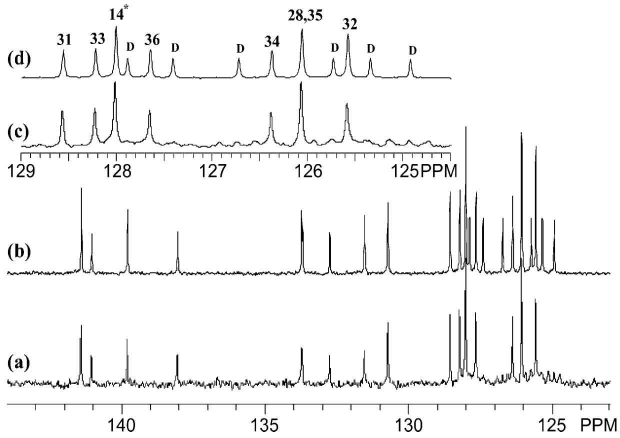

FIGURE 3. ^{13}C NMR spectra (125 MHz): (a) ^{13}C{^{1}H} spectrum of **2**-d_{14}; (b) ^{13}C{^{1}H,^{2}H} spectrum of **2**-d_{14}; (c) expansion of (a); (d) expansion of (b). * = two positions are equivalent through rapid dynamic averaging.

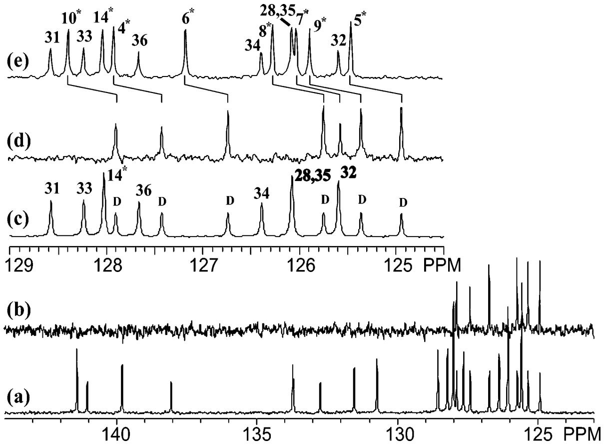

FIGURE 4. ^{13}C NMR spectra (125 MHz): (a) ^{13}C{^{1}H,^{2}H} spectrum of **2**-d_{14}; (b) ^{13}C{^{2}H} INEPT spectrum of **2**-d_{14}; (c) expansion of (a); (d) expansion of (b); (e) ^{13}C{^{1}H} spectrum of **2** showing correlation with (d) arising from ^{2}H isotope shifts. * = two positions are equivalent through rapid dynamic averaging.

Two 2-D heteronuclear data sets are crucial to making full ^{1}H and ^{13}C assignments in **2**. The ^{1}H−^{13}C inverse heteronuclear

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(20) Rinaldi, P. L.; Baldwin, N. J. *J. Am. Chem. Soc.* **1983**, *105*, 7523−7527.

TABLE 2. ^{13}C NMR Assignments for 1,3-Bis(1-naphthyl)-5-(2-naphthyl)benzene (2)

carbon	δ (ppm)[a]	int.[a]
C-11,C-13	141.41	2.2
C-15	141.03	1.0
C-1,C-17	139.92	1.9
C-27	138.04	1.0
C-3,C-19	133.87	2.0
C-29	133.68	1.0
C-30	132.73	1.0
C-2,C-18	131.62	1.7
C-12	130.73	1.7
C-31	128.55	2.1
C-10,C-26	128.36	3.6
C-33	128.20	2.1
C-14,C-16	128.02	3.5
C-4,C-20	127.90	3.7
C-36	127.64	2.0
C-6,C-22	127.16	3.8
C-34 [or C-35]	126.37	2.0
C-8,C-24	126.24	3.8
C-28 and	126.04	3.9
C-35 [or C-34]	126.03	4.0
C-7,C-23	125.99	4.0
C-9,C-25	125.86	3.6
C-32	125.56	2.1
C-5,C-21	125.43	4.0

[a] Chemical shift (δ) and intensities from ^{13}C{^{1}H} 1-D spectra.

single-quantum correlation experiment (HSQC) correlates ^{1}H and ^{13}C signals that are coupled via one-bond coupling.[21] We used a version relying on gradient coherence transfer, gHSQC[22] (Figure S2). From this data, a number of assignments can be made. The ^{13}C assignments for 28, 14 and 16, 12, and 34 and 35 are straightforwardly made, for example, from the previous ^{1}H assignments, with additional confidence provided from the gHSQC, ^{13}C chemical shifts, and measurable $^{3}J_{H-H}$ values. Assignments for quaternary carbons, which are not observed in HSQC spectra, and ^{1}H and ^{13}C assignments for carbons bearing ^{1}H in regions of spectral congestion (31,10,26; 32,33,36; and 8,9,24,25,34,35) require additional data. The n-bond ^{1}H$-$^{13}C heteronuclear correlation experiment (gHMBC) suppresses the one-bond couplings observed in gHSQC and correlates ^{1}H and ^{13}C signals that are coupled via two- and three-bond coupling[22,23] (Figure S3). This technique enables the assignment of quaternary carbons via the correlation to nearby protons. The complementary information provided by gHSQC and gHMBC enables the unraveling of congested spectral regions.

Table 2 contains NMR assignments for **2** derived from the ^{13}C{^{1}H}, gHSQC, and gHMBC spectra. This combination of data allows the unambiguous assignment of all protons and all carbons except C-34 and C-35. Due to the strong second-order coupling of H-34 and H-35, and the near-equivalence of H-33 and H-36, no compelling evidence was obtained that allows unambiguous assignments of C-34 and C-35. Data from similar compounds suggest C-34 would be chemically shifted slightly downfield, but this assignment is left as tentative in Table 2.

A crucial factor in utilizing the long-range ^{1}H$-$^{13}C HMBC data in aromatic compounds such as **2** and **2**-d_{14} is the fact that aromatic three-bond ^{1}H$-$^{13}C couplings, $^{3}J_{H-C}$, range from 7 to 10 Hz, whereas aromatic two-bond couplings are typically much smaller, $^{2}J_{H-C} < 4$ Hz.[24] Strong (s) and very strong (vs) couplings in the gHMBC spectra, optimized to $^{n}J_{H-C} = 8$ Hz, of **2** and **2**-d_{14} can therefore be attributed exclusively to three-bond connectivities.

TABLE 3. ^{13}C NMR Assignments for 1,3-Bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (2-d_{14})

carbon	δ (ppm)[a]	int.[a]
C-11,C-13	141.41	2.0
C-15	141.04	1.0
C-1,C-17	139.79	1.5
C-27	138.05	1.0
C-3,C-19	133.73	1.5
C-29	133.69	1.0
C-30	132.74	1.0
C-2,C-18	131.53	1.5
C-12	130.72	2.0
C-31	128.55	2.3
C-33	128.22	2.4
C-14,C-16	128.00	4.1
C-10[b]	127.89 HD	1.3
C-36	127.64	2.3
C-4[b]	127.41 HD	1.3
C-6[b]	126.72 HD	1.3
C-34 [or C-35]	126.37	1.9
C-28	126.051	2.0
C-35 [or C-34]	126.049	2.0
C-8[b]	125.73 HD	1.3
C-32, C-7[b]	125.58	3.1
C-9[b]	125.34 HD	1.3
C-5[b]	124.92 HD	1.3

[a] Chemical shift (δ) and intensities from ^{13}C{^{1}H,^{2}H} 1-D spectra. Resonances labeled "HD" observed only with simultaneous ^{1}H and ^{2}H decoupling, or in the ^{13}C{^{2}H} INEPT spectrum. [b] Assignments are based on assignments of **2**, in conjunction with ^{2}H isotope shifts (Table 4).

TABLE 4. ^{2}H Isotope Shifts on ^{13}C NMR Chemical Shifts in 1,3-Bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (2-d_{14})

carbon	δ_D (ppm)	$\delta_D - \delta_H$[a]	bonding[b]
C-1,C-17	139.79	−0.13	1*o* + 2*m*
C-3,C-19	133.73	−0.14	2*o* + 3*m*
C-2,C-18	131.53	−0.09	1*o* + 4*m*
C-10,C-26	127.89	−0.47	1*i* + 1*o* + 2*m*
C-4,C-20	127.41	−0.49	1*i* + 1*o* + 2*m*
C-6,C-22	126.72	−0.44	1*i* + 1*o* + 1*m*
C-8,C-24	125.73	−0.51	1*i* + 2*o* + 1*m*
C-7,C-23	125.58	−0.41	1*i* + 1*o* + 1*m*
C-9,C-25	125.3	−0.52	1*i* + 2*o* + 1*m*
C-5,C-21	124.9	−0.51	1*i* + 2*o* + 0*m*

[a] ^{2}H isotope shift on ^{13}C NMR resonance = δ (**2**-d_{14}) − δ (**2**). [b] ^{2}H isotopes influencing an individual ^{13}C NMR resonance: *i* = *ipso*, *o* = *ortho*, *m* = *meta*.

Table 3 contains NMR assignments for 1,3-bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (**2**-d_{14}) derived from the ^{13}C{^{1}H}, ^{13}C{^{1}H,^{2}H}, ^{13}C{^{2}H} INEPT, gHSQC (Figure S4), and gHMBC (Figure S5) spectra. Assignments for carbons bearing ^{2}H were derived from the ^{13}C{^{2}H} INEPT spectrum (Figure 4). These carbons were then correlated to the fully assigned ^{13}C{^{1}H} spectrum of the protio isotopomer **2** through consideration of the expected ^{2}H isotope shifts (Figure 4e, Table 4). The directly

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bonded *ipso*-^{2}H produces an upfield shift of ~0.3 ppm (to lower frequency), and each *ortho*-^{2}H contributes an additional upfield shift of ~0.1 ppm. *meta*-^{2}H makes little contribution.

Summary

Molecular glass-forming materials 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**) and 1,3-bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (**2**-d_{14}) have been synthesized in gram quantity and high purity using Suzuki coupling chemistry. Sophisticated triple resonance and two-dimensional NMR measurements permit the detailed assignment of ^{1}H, ^{2}H, and ^{13}C NMR spectra. Dynamic averaging of the atropisomers of these tris(naphthyl)benzene derivatives is rapid on the NMR time scale at room temperature. The availability of both protio- and deuterio-isotopomers of tris(naphthyl)benzene **2** has enabled a series of important investigations concerning diffusion in glasses and the physical properties of glassy materials.[13−15]

Experimental Section

$CuBr_2$ Adsorbed on Alumina.[18] Alumina (80 g, neutral, Activity I) and water (120 mL) were combined with $CuBr_2$ (41 g, 183 mmol). The green suspension was mixed for 4 h using a rotary evaporator (without vacuum). The water was then removed, first by rotary evaporation at 80 °C under aspirator vacuum, followed by mechanical vacuum (0.1 mmHg) at 65 °C overnight to obtain the reagent as a black solid.

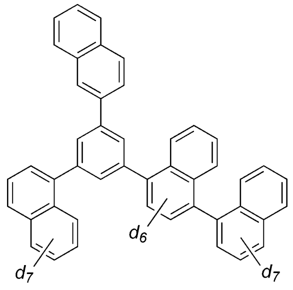
1-Bromonaphthalene-d_7 (6-d_7).[18] Naphthalene-d_8 (**5**-d_8) (4.99 g, 36.6 mmol) and $CuBr_2$ adsorbed to alumina (120 g) were added to CCl_4 (250 mL). The solution was stirred (mechanical stirrer) for 9 days at 25−29 °C, and the reaction progress was followed by GC/mass spectrometry (single ion method). The mixture was filtered, the filter cake was rinsed with CCl_4 (100 mL), and the filtrate was concentrated to a pale yellow oil by rotary evaporation. Residual naphthalene was removed by sublimation. Distillation afforded a short forerun, followed by the desired product **6**-d_7 as a pale yellow oil at 78 °C (head temperature, 0.1 mmHg). 6.02 g (77%). ^{2}H NMR (76.74 MHz, $CHCl_3$) δ 7.32 (s, 1D), 7.57 (d, 2D), 7.82 (m, 3D), 8.25 (s, 1D).

1-Naphthylboronic Acid-d_7 (9-d_7).[25] 1-Bromonaphthalene-d_7 (**6**-d_7) (6 g, 28 mmol) was added to THF (41 mL), and the solution was cooled to −78 °C under N_2. *n*-BuLi (2.35 M in hexanes, 13.1 mL, 30.9 mmol) was added dropwise, maintaining the temperature below −60 °C. After the solution had stirred for 50 min, a separate solution of $B(OMe)_3$ (6.6 mL, 57.8 mmol) and THF (32 mL) was cooled to −78 °C and then added slowly, maintaining the temperature below −60 °C. The solution was allowed to warm to room temperature overnight while stirring. The next day the reaction mixture was cooled to 5 °C, and concentrated HCl (11.1 mL) was added slowly. The solution was stirred at room temperature for 1 h. Water (165 mL) was added, and the solution was extracted with ether (3 × 280 mL). The combined ether extracts were dried with $MgSO_4$, and the solvent was removed using rotary evaporation to yield an off-white solid. The solid was collected into a filter funnel and washed with benzene (4 × 55 mL). After air-drying for 1.5 h, 1-naphthylboronic acid-d_7 (**9**-d_7) was collected as a white solid (3.13 g, 62% yield): ^{1}H NMR (Me_2SO-d_6) δ 8.38 (s, 2H); ^{2}H NMR (38.4 MHz, Me_2CO) δ 7.47 (s (br), 3D), 7.89 (s (br), 3D), 8.61 (s (br), 1D).

1,3-Dibromo-5-(2-naphthyl)benzene (12).[12] A solution of 2-naphthylboronic acid (**11**) (1.86 g, 10.8 mmol), 1,3,5-tribromobenzene (**10**) (3.40 g, 10.8 mmol), 2 M Na_2CO_3 (10.8 mL), EtOH (11 mL), and toluene (65 mL) was stirred under N_2. After 20 min, $Pd(PPh_3)_4$ (540 mg, 4.33 mol %) was added and the solution was refluxed at 85 °C for 22 h. The solution was allowed to cool to room temperature, added to water (200 mL), and extracted with benzene (2 × 200 mL). The benzene extracts were washed with brine (250 mL) and dried with $MgSO_4$, and solvent was removed to give a light yellow oil (5.83 g). This material was purified by column chromatography (silica, 8:1 hexane/CH_2Cl_2, $R_f = 0.58$) to yield **12** as a white solid (2.49 g, 65% yield): mp 120−121 °C; ^{1}H NMR ($CDCl_3$) δ 7.52 (m, 2H), 7.64 (m, 2H), 7.77 (d, $J = 2$ Hz, 2H), 7.88 (m, 3H), 7.97 (s (br), 1H); ^{13}C NMR δ 123.6, 125.1, 126.5, 126.86, 126.9, 127.9, 128.5, 129.1, 129.4, 132.9, 133.3, 133.7, 135.8, 145.0; mass spectrum *m*/*z* (rel intensity) 364 (M^+, 50), 362 (M^+, 100), 360 (M^+, 51), 354(19), 282 (11), 202 (84), 176(11), 152 (10), 101 (42); HRMS calcd for $C_{16}H_{10}{}^{79}Br_2$ 359.9149, found 359.9162.

1,3-Bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (2-d_{14}).[12] A solution of 1,3-dibromo-5-(2-naphthyl)benzene (**12**) (1.69 g, 5 mmol), 1-naphthylboronic acid-d_7 (**9**-d_7) (1.98 g, 11 mmol), 2 M Na_2CO_3 (10 mL), EtOH (15 mL), and toluene (60 mL) was stirred under N_2. After 20 min, $Pd(PPh_3)_4$ (405 mg, 0.35 mmol, 7.0 mol %) was added and the solution was refluxed at 87 °C for 23 h. The solution was allowed to cool to room temperature and added to water (160 mL) and CH_2Cl_2 (150 mL). The organic phase was separated, and the aqueous phase was extracted three more times with CH_2Cl_2 (1 × 100 mL, 2 × 75 mL). The organic extracts were combined and dried with $MgSO_4$, and solvent was removed (30 °C under reduced pressure) to give 4.02 g of a light brown solid. This material was purified via flash column chromatography[26,27] (silica, hexane/CH_2Cl_2, solvent gradient: 100:0 to 9:1, $R_f = 0.07$) and recrystallized from hexane to yield 1,3-bis(1-naphthyl-d_7)-5-(2-naphthyl)benzene (**2**-d_{14}) as a white solid (1.16 g, 53% yield): mp 192−193 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.69 (t, $J = 1.4$ Hz, 1H), 7.87 (m, 3H), 7.94 (d, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 1.7$ Hz, 2H), 8.18 (d, $J = 1$ Hz, 1H). ^{2}H NMR (76.8 MHz, $CHCl_3$) δ 7.70 (m, 14D); ^{13}C NMR (125 MHz, $CDCl_3$) δ 125.6, 126.049, 126.051, 126.4, 127.6, 128.0, 128.2, 128.6, 130.7, 131.5, 132.7, 133.69, 133.73, 138.1, 139.8, 141.0, 141.4; mass spectrum *m*/*z* (rel intensity) 470 (M^+, 51), 446 (8), 393 (21), 322 (77), 238 (57), 236 (56), 210 (24), 208 (25), 157 (66), 129 (100), 128 (75); HRMS calcd for $C_{36}H_{10}D_{14}$ 470.2757, found 470.2752.

In one instance, the mass spectrum of the product contained a high-mass peak at $m/z = 602$, in addition to the expected parent ion for **2**-d_{14} at $m/z = 470$.



13-d_{20}

We speculate that the peak at $m/z = 602$ arises from the binaphthyl-containing structure **13**, which may ultimately result from carrying a minor impurity of 1,4-dibromonaphthalene-d_6 through the synthetic sequence.

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[26] Because of the poor solubility of the sample in the solvent used for column chromatography, an alternate method of loading the sample was used. The sample was dissolved in CH_2Cl_2 and mixed with a portion of silica gel (1:5 ratio of sample to silica gel). The mixture was evaporated to dryness and loaded atop the chromatography column.

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Acknowledgment. We thank the National Science Foundation for financial support (R.J.M., NSF-0412707; M.D.E., NSF-0605136; Departmental NMR facilities, NSF-0342998). We thank Kimberly S. Petersen for assistance with the synthesis of 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**), Dr. Monika Ivancic for assistance with ^{2}H NMR spectroscopy, and Prof. Hans J. Reich for helpful discussions.

Supporting Information Available: Improved procedure for the synthesis of 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**). NMR spectra (600 MHz): gDQ-COSY, ^{1}H,^{13}C-gHSQC, ^{1}H,^{13}C-gHMBC for compound **2**; gDQ-COSY, ^{1}H,^{13}C-gHSQC, ^{1}H,^{13}C-gHMBC, ^{2}H (1-D) for compound **2**-d_{14}; scanned copies of 1-D ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO701921M