

Molecular Compasses and Gyroscopes with Polar Rotors: Synthesis and Characterization of Crystalline Forms

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Abstract: We report the highly convergent synthesis and solid-state characterization of six crystalline "molecular compasses" consisting of a central phenylene rotor with polar substituents, or compass needle, and two trityl groups axially connected by acetylene linkages to the 1,4-positions. Compounds with fluoro-, cyano-, nitro-, amino-, diamino-, and nitroamino substituents are expected to emulate the parent compound which was shown to form crystals where the central phenylene can rotate about its 1,4-axis with rate constants in the $10^3 - 10^6 \text{ s}^{-1}$ dynamic ranges near ambient temperature, depending on crystal morphology. With data from single-crystal X-ray diffraction analysis, solid-state CPMAS ^{13}C NMR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), it is shown that a relatively small structural perturbation by a single polar group (F, CN, NO_2 , NH_2) results in isomorphous structures with analogous properties. In analogy to the parent compound, crystals grown from benzene formed clathrate structures in the space group $P\bar{1}$ with one molecular compass and two benzene molecules per unit cell. Solvent-free crystals with the same space group obtained by a first-order phase transition between 60 and 130°C were shown to be spectroscopically identical to those obtained by slow solvent evaporation from a mixture of CH_2Cl_2 and hexanes. A qualitative analysis of the positionally disordered phenylene groups in terms of the expected solid-state rotational dynamics suggests a nonsymmetric, 2-fold rotational potential, or a process involving full 360° turns.

1. Introduction

In search of photonic materials with electrooptic and dielectric functions based on the rotational dynamics of internal dipoles,^{1,2} we recently made progress on the preparation of solids built with molecules having structures and functions that are analogous to those of macroscopic compasses and gyroscopes. Like these navigational devices, the desired structures are characterized by rigid frameworks that shield reorienting or rotating polar groups capable of responding to external electromagnetic fields and to forces causing changes in its angular momentum. We have shown that compounds with axially substituted arylene rotors linked by two acetylenes to triarylmethyl³ and triptycyl⁴ frameworks are promising candidates (Figure 1). Since rotation about alkyne-aryl single bonds in the ground state is essentially frictionless,³⁻⁵ we expect that triarylmethanes and triptycenes with bulky substituents or bridging groups will provide the steric

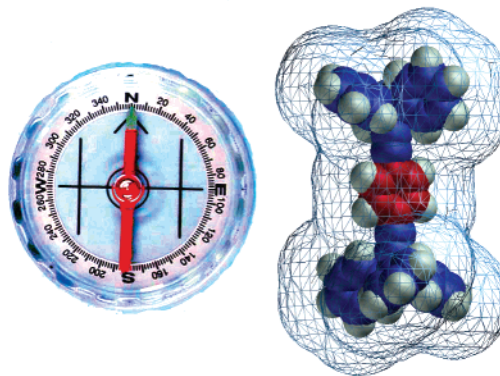


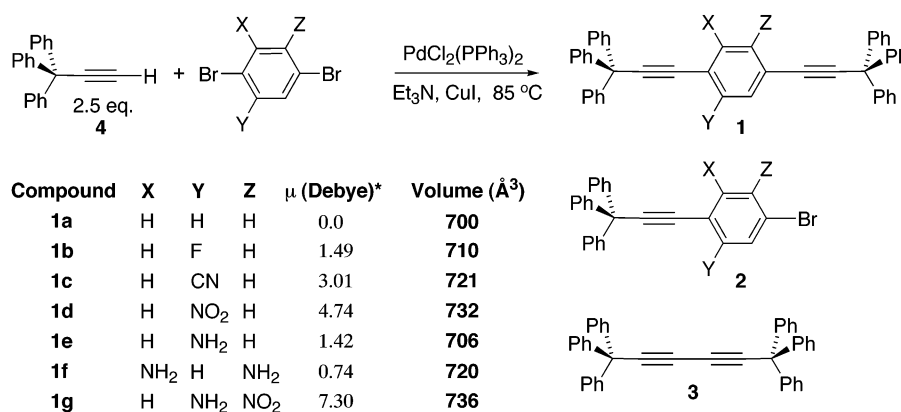
Figure 1. Suggested analogy between a macroscopic compass and 1,4-bis(triphenylpropynyl)benzene (**1a**), a molecule with a triarylmethane framework (blue) and a phenylene rotor (red). The space-filling model of **1a** is shown with a 4 Å solvent-accessible surface.

shielding required to prevent contacts between the arylene rotor and neighboring molecules in the solid state. With a combination of variable temperature ^{13}C CPMAS NMR and quadrupolar echo ^2H NMR line-shape analysis, we recently showed that crystals of 1,4-bis(3,3,3-triphenylpropynyl)benzene (**1a**)⁶ display the

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- (1) (a) Salech, B. E. A.; Teich, M. C. *Fundamentals of Photonics*; Wiley-Interscience: New York, 1991. (b) Weber, M. J. *Handbook of Optical Materials*; CRC Press: Boca Raton, 2002. (c) Kasap, S. O.; Kasap, S. O. *Optoelectronics and Photonics: Principles and Practices*; Prentice Hall: New York, 2001. (d) Setian, L. *Applications in Electrooptics*; Prentice Hall: New York, 2001.
- (2) Hench, L. L.; West, J. K. *Principle of Electronic Ceramics*; John Wiley & Sons: New York, 1990.
- (3) Dominguez, Z.; Dang, H.; Strouse, M. J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 2398–2399.
- (4) Godínez, C. E.; Zepeda, G.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 4701–4707.

- (5) (a) Saebo, S.; Almlof, J.; Boggs, J. E.; Stark, J. G. *J. Mol. Struct. (THEOCHEM)* **1989**, *200*, 361–373. (b) Abramov, A. V.; Almenningen, A. Cyvin, B. N.; Cyvin, S. J.; Jonvik, T.; Khaikin, L. S.; Rommingen, C.; Vilkov, L. V. *Acta Chem. Scand.* **1988**, *A42*, 674–678. (c) Sipachev, V. A.; Khaikin, L. S.; Grikina, O. E.; Nikitin, V. S.; Traettberg, M. *J. Mol. Struct.* **2000**, *523*, 1–22.

Scheme 1^a

^a Asterisk denotes that dipole moments and molecular volumes were calculated from structures optimized with the AM1 method as implemented by the program Spartan.

desired rotation. Despite the relatively modest shielding offered by simple triphenylmethyl (trityl) groups (Figure 1 and Scheme 1), the phenylene rotor was shown to undergo a 2-fold flipping motion in the solid state with rate constants in the MHz regime near ambient temperature. Analogous structures have been recently suggested by Glass et al.⁷ as scaffolds for pinwheel fluorescence sensors in solution and by Joachim et al. for the construction of molecular “barrows” guided and driven by AFM tips on atomically smooth surfaces.⁸ As a continuation of our studies on materials based on molecular compasses and gyroscopes, we report here the synthesis, characterization, and solid-state properties of several analogues of **1a** with phenylene groups possessing fluoro- (**1b**), cyano (**1c**), nitro (**1d**), amino (**1e**), *o*-diamino (**1f**), and *p*-nitroamino (**1g**) substituents (Scheme 1). The primary goal of this work is to determine the effects of polar rotors on the crystallization of molecular compasses and gyroscopes with simple trityl frames and to test a suitable synthetic procedure. While the magnitudes of dipole moments calculated by the AM1 method for compounds **1b–1g** range from 0.74 to 7.30 (Scheme 1), their calculated molecular volumes differ by less than 5% from that of **1a**. Knowing that crystallization of apolar molecules is determined by weak van der Waals forces which manifest in the form of volume-filling, close-packing interactions,^{9,10} one may expect homologous series such as that given by **1a–1g** to form isomorphous crystal structures. Noting that the introduction of polar substituents on the phenylene group of **1a** makes the analogy to macroscopic compasses closer, one may suggest that the “box” of the compass will remain constant while the nature of the “needle” inside would be systematically varied. Unless unusual dipole–dipole interactions were to be manifested, the corresponding crystals should have analogous packing arrangements. At the same time, knowing that rapid reorientation of the phenylene group occurs in crystals of **1a**, it seems possible that analogous dynamics may be observed in crystals of **1b–1g**. In addition to the synthesis and solution characterization of compounds **1b–1g**, we analyze here the relation between their various crystal

structures with a combination of X-ray diffraction, high-resolution solid-state ¹³C CPMAS NMR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The results reported in this paper confirm the expected solid-state isomorphism with various degrees of positional disorder.^{9,10}

2. Results and Discussion

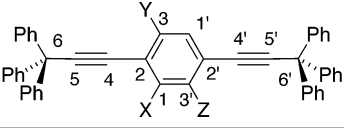
2.1. Synthesis. Molecular compasses **1b–1g** were synthesized by a double-coupling reaction with 2.5 equiv of 3,3,3-triphenyl-1-propyne and the corresponding *p*-phenylene bromide in a manner that is analogous to that reported previously for compound **1a** (Scheme 1).^{3,6} Samples of 3,3,3-triphenyl-1-propyne were obtained from the reaction of trityl chloride with ethynylmagnesium bromide in benzene at ambient temperature.^{7,11} Molecular compasses **1b**, **1d**, and **1e** were prepared with commercially available 2,5-diiodofluorobenzene, 2,5-dibromonitrobenzene, and 2,5-dibromoaniline, respectively. Samples of the 2-substituted 1,4-dibromophenylenes for the synthesis of molecular compasses **1c** and **1g**, and 2,3-diamino-1,4-dibromophenylene **1f**, were prepared by reported procedures (Scheme 2). 2,5-Dibromobenzonitrile was prepared by Friedel–Crafts bromination of benzonitrile as reported by Pearson et al. (Scheme 2a).¹² Our isolated yields were significantly lower than those reported by these authors (79%) but were in agreement with those recently reported by Gray et al. (12%).¹³ Samples of 3,6-dibromo-1,2-phenylenediamine were prepared in good yields in a three-step procedure from *o*-phenylenediamine (Scheme 2b).¹⁴ A clean, high-yielding, and regioselective dibromination was accomplished through a 2,1,3-benzothiadiazole obtained by condensation of the *o*-diamine with SOCl₂ in the presence of pyridine and subsequent reductive removal of sulfur with NaBH₄ regenerated the diamine. The preparation of 2,5-dibromo-4-nitroaniline was accomplished in good yields from commercial 2,5-dibromoaniline by the sequence reported by Moroni et al. (Scheme 2c).¹⁵

The Pd(0)-catalyzed reactions were carried out at 85 °C for 20 h with PdCl₂(PPh₃)₂, PPh₃, and CuI in Et₃N. The double-

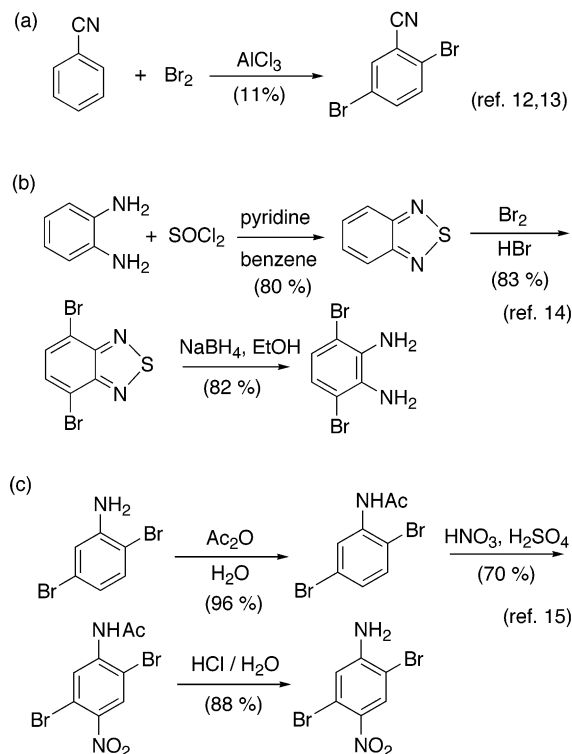
- (6) Dominguez, Z.; Dang, H.; Strouse, J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 7719–7727.
- (7) Raker, J.; Glass, T. E. *Tetrahedron* **2001**, *57*, 10233–10240.
- (8) Joachim, C.; Tang, H.; Moresco, F.; Rapenne, G.; Meyer, G. *Nanotechnology* **2002**, *13*, 330–335.
- (9) Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.
- (10) Vainshtein, B. K.; Fridkin, V. M.; Indenbom, V. L. *Structure of Crystals*; Springer-Verlag: Berlin, 1982; Vol. II.

- (11) Masson, J.-C.; Quan, M. L.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1968**, *3*, 1085–1088.
- (12) Pearson, D. E.; Stamper, W. E.; Suthers, B. R. *J. Org. Chem.* **1963**, *28*, 3147–3149.
- (13) Gray, G. W.; Lacey, D.; Hird, M.; Toyne, K. J. *PCT Int. Appl.* **1989**.
- (14) (a) Tsubata, Y.; Suzuki, T.; Miyashi, T. *J. Org. Chem.* **1992**, *57*, 6749–6755. (b) Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629–633.
- (15) Moroni, M.; Le Moigne, J.; Pham, T. A.; Bigot, J. Y. *Macromolecules* **1997**, *30*, 1964–1972.

Table 1. ^1H NMR Chemical Shift Assignments of Molecular Compasses **1a–1g**^a

							
signal	1a ^b	1b Y = F (J_{HH} , Hz)	1c Y = CN (J_{HH} , Hz)	1d Y = NO ₂ (J_{HH} , Hz)	1e Y = NH ₂ (J_{HH} , Hz)	1f X, Z = NH ₂	1g Y = NH ₂ Z = NO ₂
1	7.42	7.46 (7.6)	7.58 (8.2)	7.65 (8.2)	7.30 (7.6)	6.86	8.25
3	7.42						
1'	7.42	7.28 ^c	7.80 (1.5)	8.18 (1.5)	6.86 (1.5)		6.88
3'	7.42	7.28 ^c	7.67 (8.2, 1.5)	7.69 (8.2, 1.5)	6.84 (7.6, 1.5)	6.86	

^a Spectra were measured at ambient temperature in CD₂Cl₂. ^b Reference 6. ^c Signals overlap with the *o*- and *m*-hydrogens of the trityl group.

Scheme 2

coupling reaction proceeded to completion in all cases, with the exception of those carried out with 2,5-dibromo-4-nitroaniline (X = H, Y = NH₂, Z = NO₂) which failed to give compound **1g** under these conditions (see below). Small amounts of the known dimer **3** were also isolated along with the desired molecular compasses in the case of reactions leading to compounds **1b–1f**. Purification was carried out in all cases by column chromatography with silica gel using a mixture of CH₂-Cl₂:C₆H₆:C₆H₁₄ = 10:10:80 as the eluent. Although isolated yields under these nonoptimized conditions oscillated between 10 and 40%, molecular compasses prepared by stepwise coupling proceeded in higher overall yields (70–80%). The rate of formation of the nitroaniline molecular compass **1g** differed substantially from that of the others. Reaction conditions such as those used for the synthesis of compounds **1a–1f** yielded primarily the monocoupling product **2** (Y = NH₂, Z = NO₂) with small amounts of **1g** and alkyne dimer **3**. The regioselectivity of the monocoupling reaction was established by a 2D heteronuclear chemical shift correlations via multiple bond connectivities (HMBC).¹⁶ A rapid monocoupling reaction at the

bromide that is *ortho* to the nitro group and *para* to the aniline is in agreement with expectations from the effects of substituents on similar alkyne–aryl coupling reactions.¹⁷ However, a one-step double-coupling preparation of compound **1g** was accomplished with an excess of 3,3,3-triphenylpropyne and longer reaction times.

2.2. Spectroscopic Characterization. The characterization of molecular compasses **1b–1g** was carried out at ambient temperature by ^1H NMR, ^{13}C NMR, and HMBC analyses. High-resolution mass spectra from electron impact ionization gave relatively abundant parent ions. Analysis by FT-IR revealed very weak or unobservable stretching bands for the triple bonds in all six rotors. Diffraction-quality single crystals were only obtained in the cases of the fluoro- (**1b**), cyano- (**1c**), nitro- (**1d**), and amino-substituted (**1e**) molecular compasses. No suitable crystals could be obtained for the diamino (**1f**) and nitroamino (**1g**) rotors.

As expected for structures that only have aromatic hydrogens, the ^1H NMR signals in CD₂Cl₂ appear in all cases in a very small range (less than 2 ppm). Although hydrogen signals corresponding to the trityl groups are observed as broad multiplets, signals corresponding to hydrogens of the substituted phenylenes could be assigned in most cases. A summary of chemical shift data corresponding to the ^1H NMR signals of the substituted phenylene groups is included in Table 1 and the corresponding ^{13}C NMR data in Table 2. The atom numbering used in Tables 1 and 2 is illustrated in the first table, which corresponds to the numbering used in a later section to describe the X-ray structures. Signals corresponding to hydrogen atoms that are *ortho* to the -F, -CN, -NO₂, and -NH₂ substituents in molecular compasses **1b**, **1c**, **1d**, and **1e** (H1' in Table 1) occur as doublets with a small *meta* coupling constant (4J = 1.5 Hz). Hydrogen atoms that are *meta* (C1) and *para* (C3') to the substituent share a larger *ortho* coupling constant (3J = 7.6–8.2 Hz). The *para* hydrogens at C3' occur as doublet of doublets with small and large coupling constants 4J and 3J . The diamino compound **1f** has average mirror symmetry in solution and the two protons directly bonded to the 1,4-phenylene appear as a singlet. The spectrum of compound **1g** consists of upfield and downfield singlets corresponding to hydrogens that are *ortho* to the amine and nitro groups, respectively, which are also *para* to each other.

Since the rotational dynamics of the central phenylene in crystals of **1a** fall within a time scale that is suitable for

(16) 2D HMBC spectra are reported in the Supporting Information section.

(17) Singh, R.; Just, G. *J. Org. Chem.* **1989**, *54*, 4453–4457.

Table 2. ^{13}C Chemical Shifts of Molecular Compasses **1a–1g**^a

signal	1a ^b	1b Y = F (J_{CF} , Hz)	1c Y = CN	1d Y = NO ₂	1e Y = NH ₂	1f X = Z = NH ₂	1g Y = NH ₂ , Z = NO ₂
C1	123.1	133.5 (2.0)	132.9	135.3	132.3	122.1	130.3
C2	131.3	112.3 (16)	124.3	124.6	108.4	109.6	107.6
C3	123.1	162.9 (251)	115.8	149.7	148.6	136.9	152.3
C1'	123.1	118.7 (23)	135.9	127.8	117.1	136.9	118.7
C2'	131.3	125.3 (9.5)	126.7	118.5	124.5	109.6	121.1
C3'	123.1	127.7 (4.0)	135.5	135.8	121.2	122.1	139.3
C4	84.7	84.3 (4.0)	82.0	80.9	82.5	82.8	80.1
C4'	84.7	79.0	83.4	83.3	85.8	82.8	82.2
C5, C5'	97.2	102.6 (34)	103.9	105.3	102.7	102.2	104.3, 103.6
		98.5	99.0	101.1	96.6		
C6, C6'	56.1	56.5	56.6	56.6	56.5	56.9	56.9, 57.0
		56.8	56.9	57.0	56.9		

^a Spectra measured at ambient temperature in CD_2Cl_2 . ^b Values from ref 3.

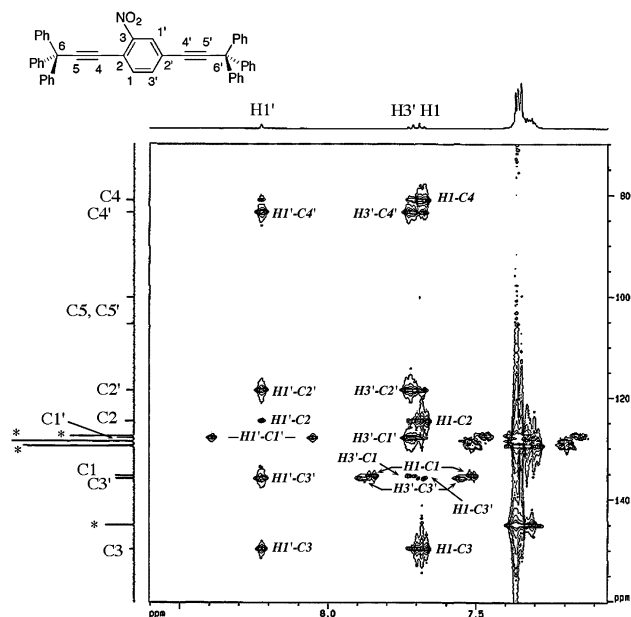


Figure 2. 500 MHz HMBC spectrum of the nitro-substituted molecular compass **1d** in CD_2Cl_2 . Signals corresponding to the trityl groups appear near 7.4 ppm in the ^1H dimension are labeled with an asterisk (*) in the ^{13}C axis.

coalescence analysis by variable temperature ^{13}C CPMAS NMR,^{3,6} we carried out a precise assignment of ^{13}C chemical shifts corresponding to polar phenylenes in compounds **1b–1g**. It is well-known that assignments from solution spectra can be useful to assign signals measured in the solid state under the ^{13}C CPMAS experiments.¹⁸ The assignment of most carbon signals was possible with HMBC measurements by taking advantage of the characteristic shielding values and coupling patterns of hydrogen atoms in the central phenylene rotors. The HMBC spectrum of compound **1d**, with a nitrophenylene rotor, is illustrated in Figure 2 as an example. Vicinal and long-range correlations between each hydrogen ($\text{H1}'$, $\text{H3}'$, and H1) and carbon nuclei of the nitrophenylene (C1–C3 and C1'–C3') and the two alkyne carbons directly attached to the ring (C4 and C4') allow for the unambiguous assignment of all the carbon signals.

A summary of the ^{13}C NMR data for compounds **1b–1g** is included in Table 2 along with chemical shift values for **1a**

which are included for comparison. Due to the presence of substituents that break the symmetry of the 1,4-phenylene in **1b–1e** and **1g**, all the carbons corresponding to the diethynylphenylenes (C1–C6 and C1'–C6') are resolved in the ^{13}C NMR spectrum. Aromatic signals assigned to the trityl groups reveal fast conformational equilibration given by a time-averaged 3-fold symmetry that renders the three phenyl groups in each trityl group equivalent and a local 2-fold symmetry that makes each phenyl group symmetric along its 1,4-axis. Eight signals are assigned to 36 aromatic trityl carbons. Multiple bond connectivity correlations by the HMBC technique were used to assign the carbons in the 1,4-phenylene groups and the alkyne carbons directly bonded to the aromatic ring of the rotors in **1c**, **1d**, **1e**, and **1g**. The corresponding spectra are reported in the Supporting Information section. Although carbon signals of the 2-fluoro-1,4-phenylene group in **1b** were not sufficiently resolved for HMBC analyses, signals of the central phenylene and alkyne carbons could be assigned from their C–F coupling constants which range from $^1J_{\text{CF}} = 251$ Hz for the *ipso* carbon, to $^3J_{\text{CF}} = 2$ and $^4J_{\text{CF}} = 4$ Hz, respectively, for the *meta* (C1) and *para* carbons (C3').

2.3. X-ray Studies: Benzene Clathrates and Solvent-Free Crystals. While polycrystalline samples could be obtained from various solvents, single crystals for structural elucidation were obtained under relatively strict conditions. Two polymorphs of **1b** could be obtained by slow evaporation from CH_2Cl_2 and from benzene. These will be referred to as **1b** (A) and **1b** (B), respectively. Crystals of **1e** were grown by slow evaporation from a mixture of hexanes and CH_2Cl_2 in a ca. 3:1 volumetric proportion. Crystals of the cyano derivative **1c** were obtained from a 3:1 mixture of hexanes and ethyl acetate and crystals from the nitro compound **1d** from saturated hot benzene solutions which were slowly cooled. We have been unable to obtain single crystals of the diamino and nitroamino compounds, **1f** and **1g**, which are suitable for X-ray diffraction analysis. Crystallographic acquisition and refinement data for compounds **1b–1d** are listed in Table 3 and their ORTEP structures illustrated in Figure 3. The structures of solvent-free crystals of **1b** (A) and **1e** were solved in the space group $P\bar{1}$ and have unit cell axes that differ by less the 0.12 Å and unit cell angles within 1°. Detailed analyses showed that they are closely related to the solvent-free crystals of **1a** described previously.⁶ Crystals of the fluoro and nitro compounds **1b** and **1d** that are grown from benzene form triclinic structures with two solvent molecules per unit cell analogous to the benzene clathrate of **1a**.⁶

(18) (a) Stejskal, E. O.; Memory, J. D. *High Resolution NMR in the Solid State: Fundamentals of CP/MAS*; Oxford University Press: Oxford, 1997. (b) Fyfe, C. A. *Solid State NMR for Chemists*; C.F.C. Press: Guelph, Ontario, 1983.

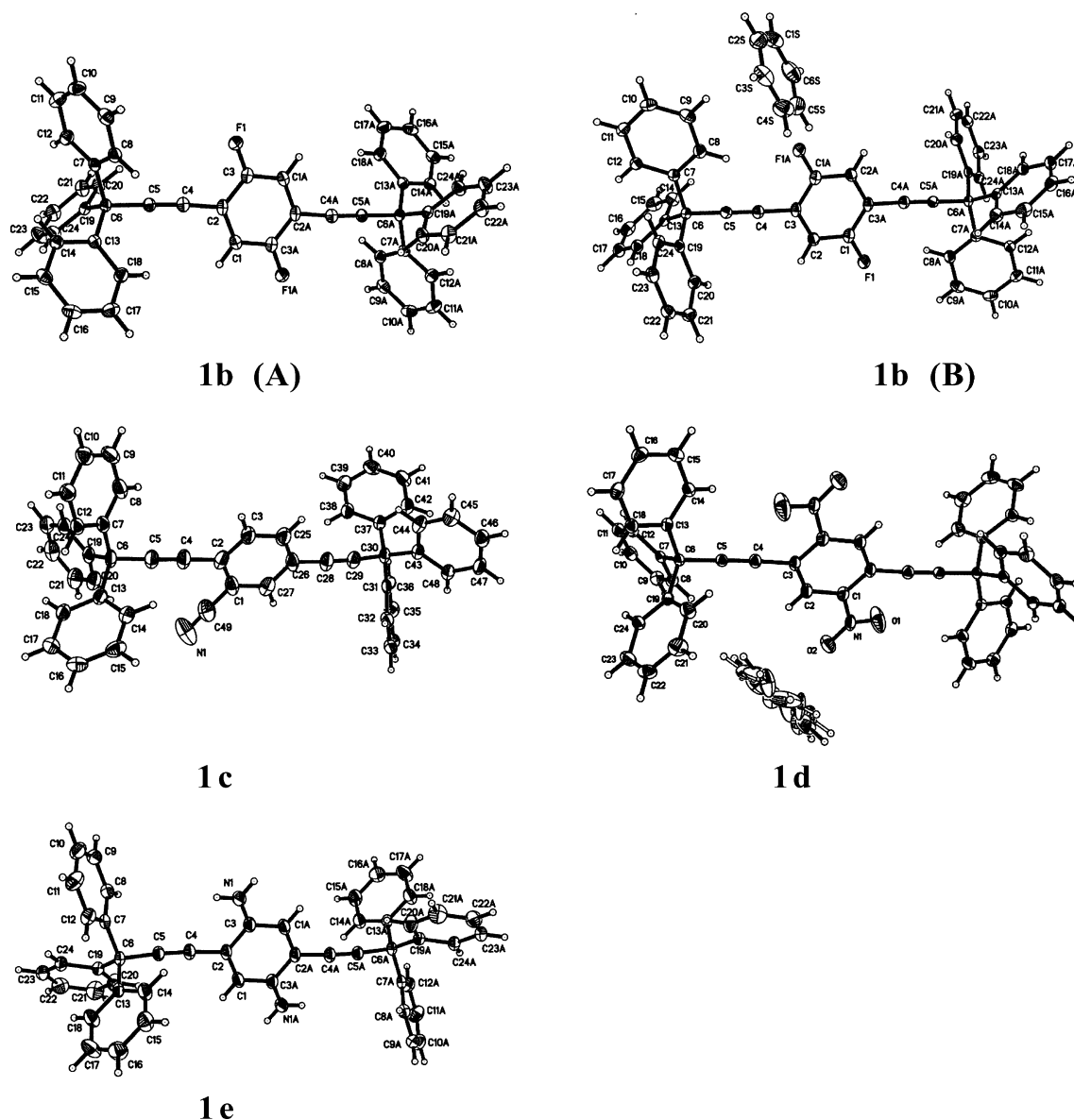
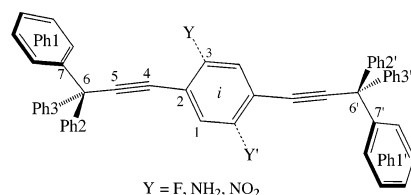


Figure 3. ORTEP diagrams of compounds **1b** (A), **1b** (B), **1c**, **1d** and **1e**. The disorder of the fluoro, amino, and nitro groups **1b**, **1e**, and **1d** is illustrated in their corresponding structures.

Table 3. Crystallographic Parameters for Molecular Compasses **1b–1e**

	molecular compass				
	1b (A)	1b (B)	1c	1d	1e
empir. form.	C ₄₈ H ₃₃ F	C ₄₈ H ₃₃ F·C ₁₂ H ₁₂	C ₄₉ H ₃₃ N	C ₄₈ H ₃₃ NO ₂ ·C ₁₂ H ₁₂	C ₄₈ H ₃₅ N
form. wt	627.74	627.74·156.09	645.76	655.25·156.09	625.77
crystal system	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1
<i>Z</i>	1	1	4	1	1
size, mm ³	0.5 × 0.2 × 0.5	0.4 × 0.3 × 0.1	0.4 × 0.3 × 0.2	0.45 × 0.3 × 0.2	0.4 × 0.3 × 0.05
color, habit	colorless prism	colorless prism	colorless prism	colorless prism	colorless prism
temp, K	100(2)	100(2)	100(2)	100(2)	298(2)
<i>a</i> , Å	9.1732(13)	8.644(2)	15.812(3)	8.4502(11)	9.2966(16)
<i>b</i> , Å	10.4607(14)	9.475(3)	20.338(4)	9.4905(12)	10.5467(18)
<i>c</i> , Å	10.4726(14)	14.530(4)	10.741(2)	14.6741(19)	10.5979(18)
α , degrees	62.126(2)	78.231(5)	90	79.925(2)	62.706(3)
β , degrees	85.744(3)	76.320(5)	94.226(4)	74.716(2)	71.071(3)
γ , degrees	71.673(2)	74.486(5)	90	76.347(2)	84.875(3)
<i>V</i> , Å ³	840.1(2)	1078.6(5)	3444.6(4)	1095.1(12)	871.3(3)
ρ_{calc} , Mg/m ³	1.241	1.207	1.226	1.230	1.193
total reflections	5519	6751	15524	7345	4726
indep. reflect.	3818	4653	4962	5075	3129
<i>R</i> (Int)	0.0120	0.0214	0.0214	0.0147	0.0169
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0407	0.0414	0.0557	0.0534	0.0389
WR2 (all data)	0.1150	0.1013	0.1521	0.1375	0.1068

Scheme 3

**Table 4.** Structural Parameters from the X-ray Structures of Compounds **1b–1e**

molecular compass	Ph1 (deg) ^a	Ph2 (deg) ^a	Ph3 (deg) ^a	d(C6–C6') (Å)	C7–C6–C2–C3 (deg)	C6'–C6–C4 (deg)	C6–i–C3 (deg)
1a^b	58.3	47.2	18.2	11.015	9.4	3.4	63
1a (C ₆ H ₆) ^b	29.8	45.1	50.5	11.012	1.8	0.1	57.8
1b (A)	58.7	44.1	19.5	11.028	14	2.9	63
1b (B)	27.0	50.2	50.4	11.032	1.0	0.4	57.8
1c^c	42.8	36.9	58.0	10.998	3.2	3.3	60.5
	–53.7	–56.4	–28.4		–13.4	7.9	59.7
1d (C ₆ H ₆) ₂	30.5	52.6	49.9	11.050	4.4	–3.2	62.4
1e	57.8	42.4	21.5	10.996	13.7	3.4	63.2

^a Dihedral angles given by the vector C5–C6 and the plane of each of the three phenyl groups. ^b Reference 6. ^c Compound **1c** has no average internal symmetry.

Compound **1c** crystallized in the monoclinic space group $P2_1/c$ with four molecules per unit cell. Crystals of compounds **1b**, **1d**, and **1e** showed positional disorder as the fluoro, nitro, and amino substituents have 50% occupancies in sites related by an average center of inversion in their crystal lattices. The average molecular structures resemble those of the *para*-disubstituted analogues with coincident crystallographic and molecular inversion centers (Figure 3). The crystal structure of **1c** is asymmetric and gives no indication of positional disorder.

While the X-ray-quality crystals of compounds **1a–1d** were obtained in three different packing structures, they share similar molecular conformations and structural distortions (Scheme 3). The two trityl groups in each molecule adopt chiral propeller conformations with opposite absolute configurations. Unlike gas-phase structures optimized by molecular mechanics (MM) and semiempirical (AM1) methods, which are predicted to have C_3 -symmetric trityl groups (not shown), the trityl groups in **1b–1d** crystallize with their phenyl groups adopting different torsion angles which give rise to asymmetric (C_1) structures. The dihedral angles formed by the σ bond between alkyne and quaternary carbons, and the plane of each of the three rings (dihedrals C5–C6–C_{ipso}–C_{ortho}, labeled Ph1–Ph3 in Table 4) vary from $\sim 20^\circ$ to $\sim 60^\circ$. The structures of compounds **1b–1d** are also characterized by having the phenyl groups projecting from the two trityl carbons in *anti* conformations (i.e., C7–C6–C6'–C7' $\approx 180^\circ$), and by having the plane of the central arylene nearly eclipsed with one of the trityl C–Ph bonds (i.e., dihedral C7–C6–C2–C3 $\approx 0^\circ$). The structures of compounds **1b–1d** present deviations from the ideally linear geometry of a substituted triple bond. Although the center of the phenylene group (labeled “i” in Scheme 3) and the two trityl carbons (C6 and C6') fall within a straight line, the four alkyne carbons deviate from that line. A measure of this deviation is given by the angle C6'–C6–C4 formed by the vector given by the two trityl carbons in the structure and the vector formed by the trityl carbon and the alkyne carbon C4. While an angle of 0° would be expected if the alkynes were linear, a deviation as large as 7.9° was noticed in **1c**. This distortion is accompanied by an in-plane rotation of the central phenylene so that the angle C6–

i–C3, where *i* is a point at the center of the substituted phenylene, takes values as large as 63.2° , when 60.0° would be expected. Structural deviations such as these have a strong effect on the rotational dynamics of macroscopic models and their potential influence on rotation of molecular compasses and gyroscopes should be kept in mind.

Packing structures of benzene-containing crystals of compounds **1b** and **1d** and solvent-free crystals of **1b** and **1c** are illustrated in Figure 4. The packing structures of benzene-grown crystals of **1b** [form B] and **1d** contain one molecular compass and two benzene molecules per unit cell. Although they are shown in Figure 4 with different choice of origin, the two structures are isomorphous with each other and with the benzene clathrate¹⁹ of **1a** reported previously.⁶ Molecular compasses reported in this study have shapes analogous to those of well-known “wheel-and-axle” and “dumbbell” structures such as 2,4-hexadiyne-1,6-diol **5**²⁰ and α,ω -diadamantylpolynes **6**²¹ (Scheme 4). These compounds are unable to form three-dimensional structures that satisfy the maximum-filling principle^{9,10,19–21} and crystals are formed with cavities and/or channels occupied by smaller molecules. As in the previously reported benzene clathrate of **1a**,^{3,6} four molecules of **1b** and **1d** make up a supramolecular cage that entraps a parallel-displaced benzene dimer (Figure 5, left). From a complementary point of view, one may describe the packing structure as having each molecular compass surrounded by six benzene dimers which form a belt around the central 1,4-diethynylphenylene (Figure 5, right). Supramolecular interactions in the structure comprise aromatic face-to-face and face-to-edge interactions²² involving solvent molecules and phenyl groups in the two trityl units. The main difference between the benzene-containing structures of **1b** and **1d** and that of **1a** comes from the positional disorder of the fluoro and nitro groups in the former two. Additionally, the benzene-containing structure of the nitro compound **1d** displays crystallographic disorder in the solvent molecules: while the coordinates of a single benzene molecule are sufficient to describe the crystal structures of **1a**, and the form B of **1b**, the refined structure of **1d** requires two sets of overlapping benzene coordinates. The centers of mass of the two crystallographically different benzene molecules are displaced by 0.178 Å and differ by a 30° rotation with respect to the 6-fold axis and by a 2.7° angle between their mean molecular planes (not shown).

Also as expected, the packing structures of the solvent-free crystals of the fluoro and amino compounds **1b** (form A) and **1e** are isomorphous with each other and with the solvent-free structures of **1a** reported previously. The packing structure of **1e** is not shown in Figure 4 but it has been included in the Supporting Information section. Analysis of the form A of **1b**

- (19) Clathrates are stoichiometric two-component crystal structures consisting of a “host” that forms a rigid lattice and a “guest” that fills interstitial positions in the same lattice. Parsonage, N. G.; Staveley, L. A. K. *Disorder in Crystals*; Oxford University Press: Oxford, 1978; Chapter 11, pp 717–798.
- (20) (a) Toda, F. In *Comprehensive Supramolecular Chemistry*; McNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6.; (b) Toda, F. *Top. Curr. Chem.* **1988**, *149*, 211–238. (c) Caira, M. R.; Nassimbeni, L. R.; Toda, F.; Vujovic, D., *J. Am. Chem. Soc.* **2000**, *122*, 9367–9372. (d) Caira, M. R.; Nassimbeni, L. R.; Toda, F.; Vujovic, D. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2119–2124.
- (21) (a) Muller, T.; Hulliger, J.; Sechter, W.; Weber, E.; Weber, T.; Wubbenhorst, M. *Chem. Eur. J.* **2000**, *6*, 54–61. (b) Weber, E.; Nitsche, S.; Wierig, A.; Csöregi, I. *Eur. J. Org. Chem.* **2002**, 856–872.
- (22) (a) Hobza, P.; Slezle, H. L.; Schag, E. W. *J. Am. Chem. Soc.* **1994**, *116*, 3500–3506. (b) Hunter, C. A.; Sanders, J. K. M., *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

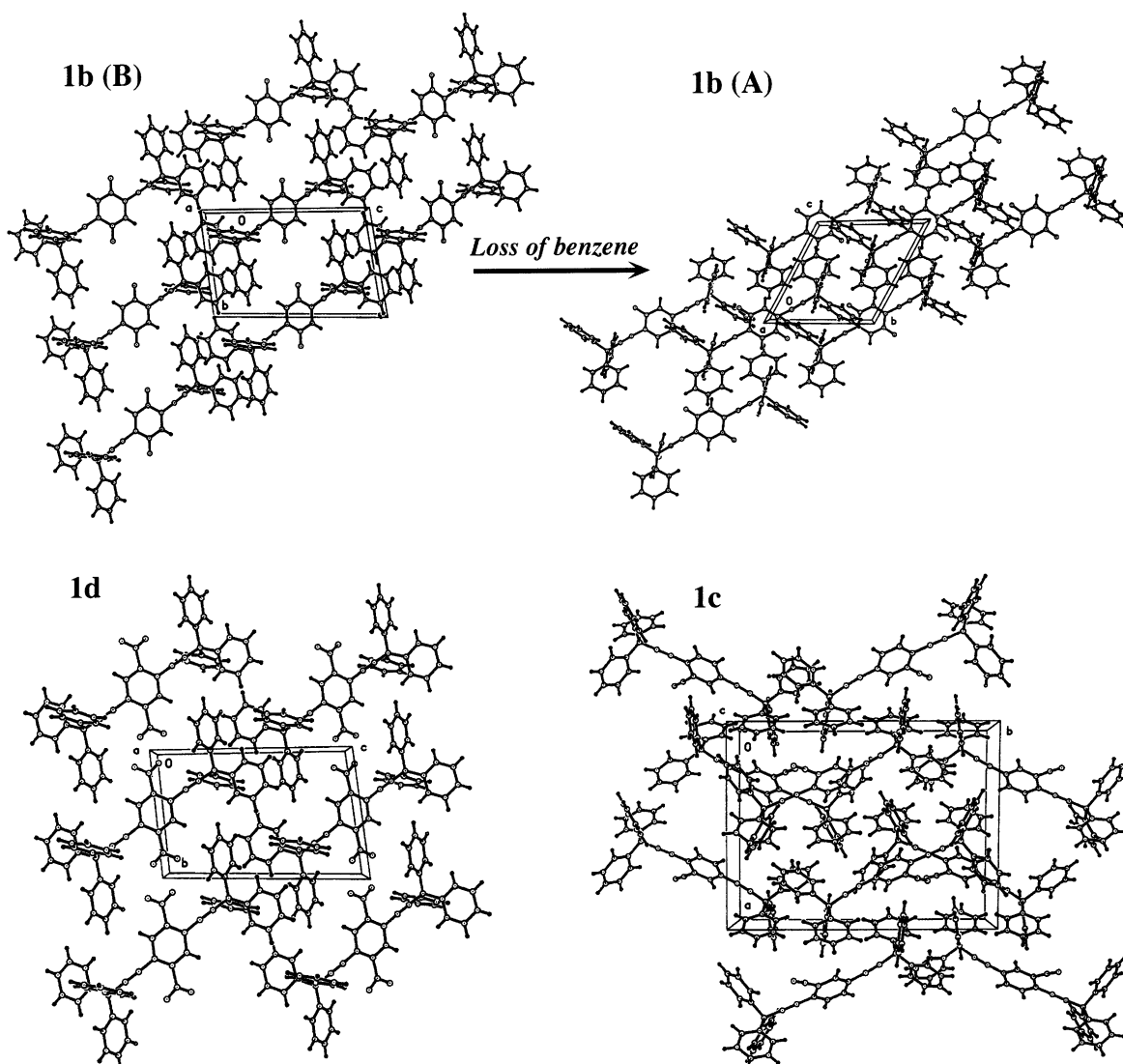
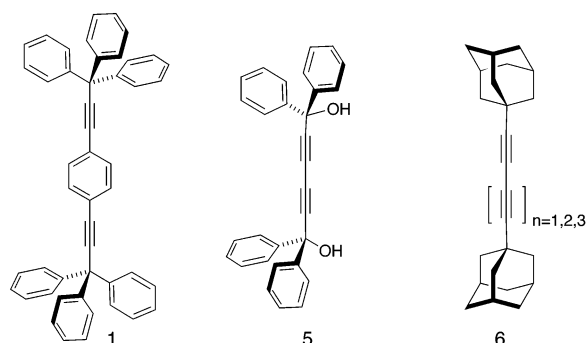


Figure 4. Top: Packing diagrams of the fluoro-substituted molecular compass **1b** its benzene clathrate, form B (right), and its solvent-free crystal, form A (left). Bottom: Packing diagram of the benzene clathrate triclinic (*P1*) structure of the nitro-substituted molecular compass **1d** (left) and packing diagram of the solvent-free monoclinic crystal form (*P2₁/c*) of the cyano compound **1c**. Parallel-displaced benzene dimers in the structures of **1b** (B) and **1d** were removed for clarity (see Figure 5).

Scheme 4



illustrates a close-packed interdigitation of the dumbbell-shaped molecules. Phenyl rings from trityl groups in six neighboring molecules fill-in the space around each phenylene. In analogy with the solvent-containing form **B**, molecules have their long axis aligned along the unit cell *b*–*c* diagonal. As it was noticed for compound **1a**, a remarkable homology between the packing structures of the benzene clathrate and the solvent-free crystals

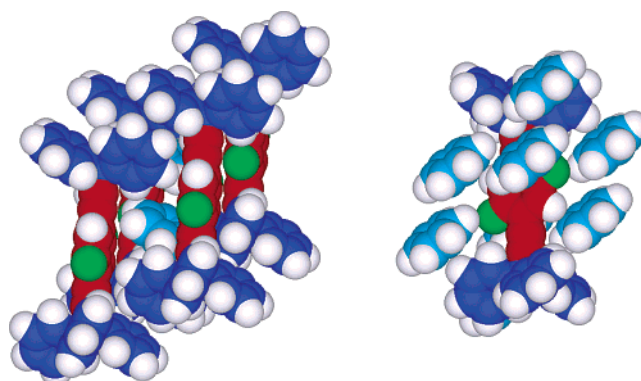


Figure 5. Space-filling models of the benzene clathrate of **1b** showing trityl groups in dark blue, the 1,4-diethynyl-2-fluorophenylene group in red, the positionally disordered fluorine in green, and benzene molecules in light blue. Left: four molecular compasses make up a supramolecular cage with a benzene dimer trapped at the center. Right: Each molecular compass is surrounded by four benzene dimers around the central portion of the molecule.

of **1b** help explain the first-order phase transition from one form to the other. A different packing structure was obtained in the

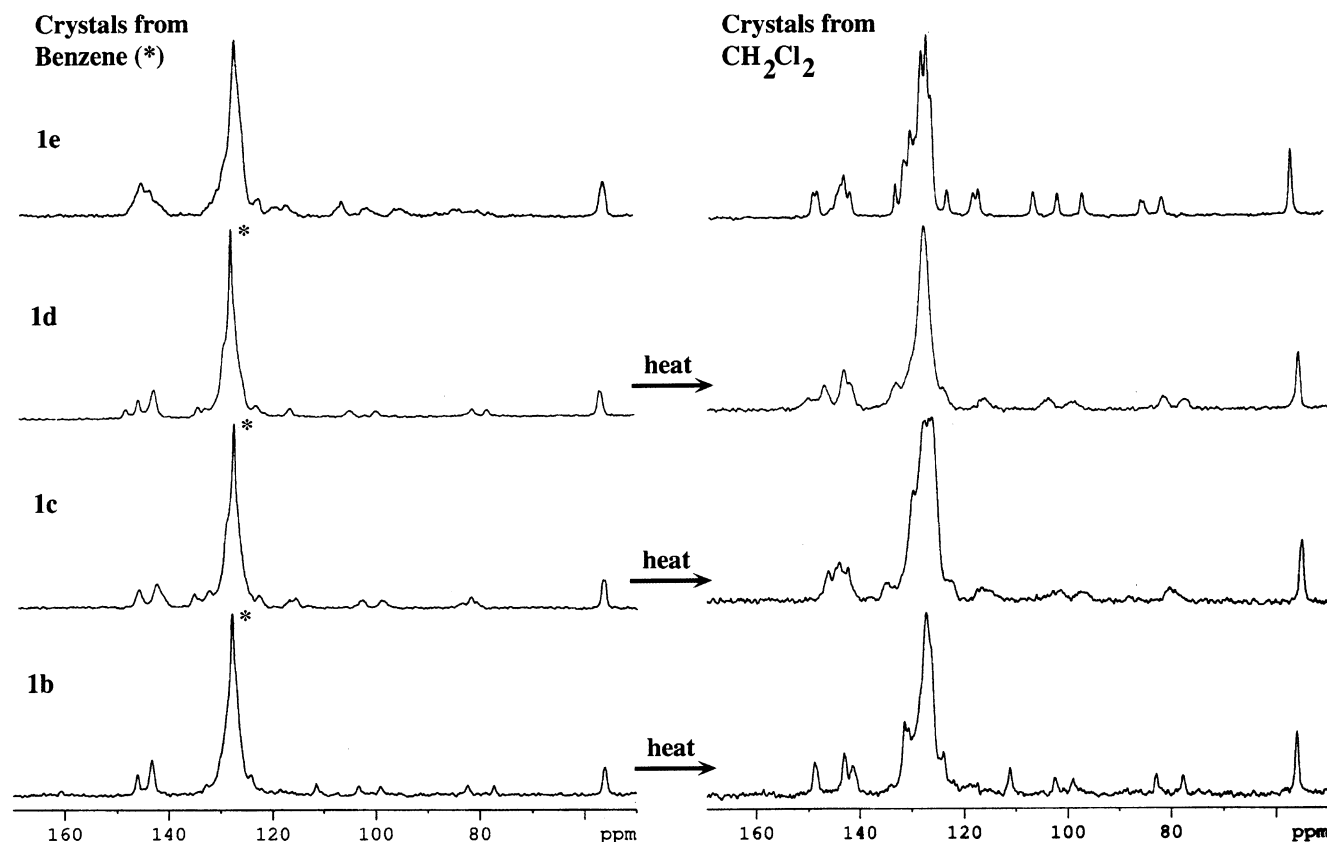


Figure 6. ^{13}C CPMAS NMR spectra measured at 300 K of crystals of **1b–1d** grown from benzene (left) and from CH_2Cl_2 (right). Benzene signals identified by dipolar dephasing experiments are marked with an asterisk (*). As indicated by the arrows, the spectra from benzene-containing crystals of **1b–1d** were transformed into the spectra obtained with crystals from CH_2Cl_2 when the samples were heated in the probe at 110 °C for 15 min. Solid samples of **1e** from benzene were solvent-free, but different from those obtained in CH_2Cl_2 .

case of the cyano-substituted compound **1c** (Figure 4). Although the structure of **1c** contains no solvent of crystallization, it differs from the solvent-free crystals of **1a**, **1b**, and **1e**. Since crystals are not disordered and there is no average inversion center, one full molecule is needed to describe the asymmetric unit and four to describe the unit cell ($Z = 4$, Table 3). Although the molecular symmetry is lower (C_1) than that observed in the crystal structures of the other compounds (C_i), the symmetry of the crystal is higher, with the monoclinic space group $P2_1/c$ (Figure 4).

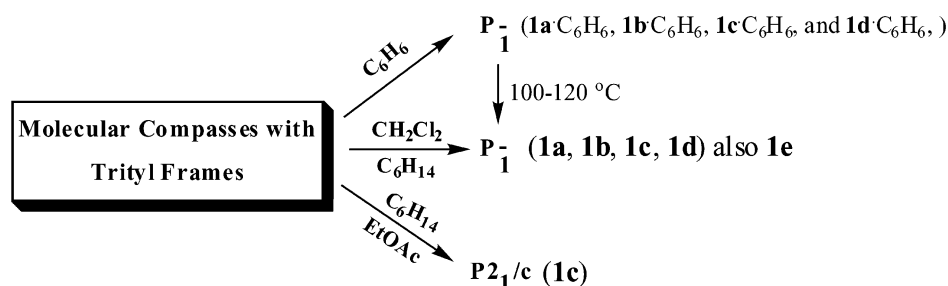
2.4. Solid-State ^{13}C CPMAS NMR: Characterization of Benzene Clathrate and Solvent-Free Structures. A relatively good correlation was observed between isotropic chemical shifts measured in solution and chemical shifts determined in the solid state by the ^{13}C CPMAS experiment. As illustrated in Figure 6, spectra were obtained with samples obtained from benzene and from CH_2Cl_2 . Not shown in Figure 6, spectra measured with samples of **1c** from ethyl acetate were different from those obtained in benzene and in CH_2Cl_2 . Signals corresponding to nonprotonated carbons, and to the highly mobile benzene molecules, could be assigned by interrupted decoupling or quaternary selection experiments.²³ In these measurements, spectra are acquired with a 50 μs interruption of the proton decoupler immediately after cross polarization and before the acquisition of the FID. Spectra measured in this manner result in the disappearance of carbon signals that experience a strong

C–H dipolar interaction, such as all the static protonated carbons. Although most aromatic signals corresponding to the central phenylene rotors overlap considerably with signals corresponding to the trityl groups, some were sufficiently resolved to suggest an assignment by analogy with the solution spectra. Four well-resolved alkyne signals between 80 and 100 ppm, observed in all spectra, reflect the substantial electronic differences between the two molecular halves that are caused by the polar substituents. However, the solid-state spectra of **1b–1e** gave no indication of distinguishable disorder sites or local domains, which appear to manifest in the form of a rather severe line broadening. As expected from the severe overlap between trityl and phenylene carbons, spectra measured with compound **1b** as a function of temperature between 213 and 373 K showed no significant spectral changes.

The ^{13}C CPMAS spectra of crystalline samples of **1b–1d** grown from benzene (Figure 6, left side) displayed a sharp peak at 128 ppm, which overlaps with signals corresponding to the *ortho* and *meta* signals of the trityl groups. It was shown that benzene-grown crystals of the cyano-substituted compound **1c** do occur as a solvent clathrate. Although we have been unable to obtain diffraction-quality single crystals to solve its X-ray structure, its thermal properties are analogous to those of the benzene clathrates from compounds **1a**, **1b**, and **1d**. As previously reported for **1a**,⁶ the ^{13}C CPMAS NMR spectra of crystals of **1b–1d** obtained from CH_2Cl_2 were identical to those obtained with benzene-grown crystals heated in situ within the NMR probe (Figure 6, right side). The monoamino derivative

(23) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697–6704.

Scheme 5

Table 5. Thermal Analysis of Molecular Compasses **1a–1g**.

compd	mp (°C)	decomp. (°C)
1a (-H)	316 (110–130) ^a	370
1b (-F)	270 (60–100) ^a	350
1c (-CN)	218 (85–130) ^a	350
1d (-NO ₂)	229 (110–140) ^a	370
1e (-NH ₂)	284 ^b	360
1f (2,3-NH ₂)	283	290
1g (2-NH ₂ -5-NO ₂)	dec	360

^a The temperature ranges in parentheses indicate the desolvation range for the benzene clathrates determined by DSC and TGA at heating rates of 10 °C/ min. ^b No clathrate was observed.

1e was the only exception among the monosubstituted molecular compasses, as the samples obtained from benzene solution have an amorphous appearance and contain no solvent in their crystal structure (Figure 6, top left spectrum).

2.5. Thermal Analysis. As summarized in Table 5, differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) carried out with freshly recrystallized samples were consistent with the ¹³C CPMAS results analyzed above. Endothermic peaks corresponding to crystal melting were observed between 218 and 284 °C for six of the compounds. Only the nitroaniline derivative **1g** decomposed before melting. Additionally, the DSC thermograms from samples of **1b–1d** grown from benzene showed a broad endothermic peak between 60 and 140 °C. That such a transition corresponds to the loss of benzene from the clathrate structure was confirmed by thermogravimetric analyses (TGA), which revealed a loss of mass corresponding to two benzene molecules per unit cell within the same temperature range. Melting transitions for crystals obtained from CH₂Cl₂, crystals from benzene desolvated in situ, and crystals grown from supercooled melts were very similar. Decomposition temperatures varied from as low as 290 °C for **1f** to as high as 370 °C for **1d**. All the monosubstituted molecular compasses **1b–1e** have melting points that are lower than that of the parent compound **1a**, perhaps reflecting a disruption to the packing structure caused by the polar substituent. Compounds **1b** and **1e** with the smallest substituents (F and NH₂) have the highest melting points and compounds **1c** and **1d** with the larger -CN and -NO₂ groups, respectively, have melting temperatures that are significantly lower (90–100 °C) than that of **1a**.

2.6. Crystallographic Disorder and Rotational Dynamics of Polar Phenylene Rotors. X-ray diffraction data, thermal analysis, and ¹³C CPMAS NMR measurements as a function of temperature show that crystals of the monosubstituted fluoro (**1b**), cyano (**1c**), nitro (**1d**), and amino (**1e**) compounds crystallize in isomorphous packing structures. Crystals grown from benzene give rise to clathrate structures in the space group *P*1̄ with one molecular compass and two solvent molecules per

unit cell and loss of solvent occurs by a first-order phase transition between 60 and 130 °C (Scheme 5). The solvent-free structures obtained in this manner are spectroscopically and thermally identical to those obtained by crystallization from mixtures of CH₂Cl₂ and hexanes. Not surprisingly, volume-filling, close-packing interactions determine the formation of isomorphous crystal structures with little or no influence by the polar groups.²⁴ In fact, a statistical analysis of crystallographic data by Whitesell et al.²⁵ and a study that considers packing indices and packing potential energies of crystalline carbonyls and nitriles by Gavezzotti²⁶ suggest that dipole–dipole interactions have little or no influence on space group symmetry and molecular orientations. However, Whitesell et al. pointed out that “this is not to say that local electrostatic interactions are not important” while Gavezzotti noted that “(dipoles) never point directly at each other, and this must be a purely electrostatic effect, since steric hindrance of the molecules would not prevent such an arrangement.” Assuming that similar arguments are valid for polar groups such as those involved in this study, the formation of local domains with adjacent dipoles adopting favorable orientations should be considered (Scheme 6). While the average X-ray structures are reminiscent of the 2,6-disubstituted-1,4-diethynylphenylenes with their polar group having 50% occupancy at the two symmetry-related sites (Scheme 6a), the formation of domains (Schemes 6b and 6c) with dipoles in adjacent molecules avoiding head-to-head interactions cannot be discounted. While information on dipolar correlation between neighboring molecules is not available from the data reported in this paper, it is expected that crystallographic disorder, whether static or dynamic, will have a strong influence on the dielectric and electrooptic properties of molecular compasses and gyroscopes.

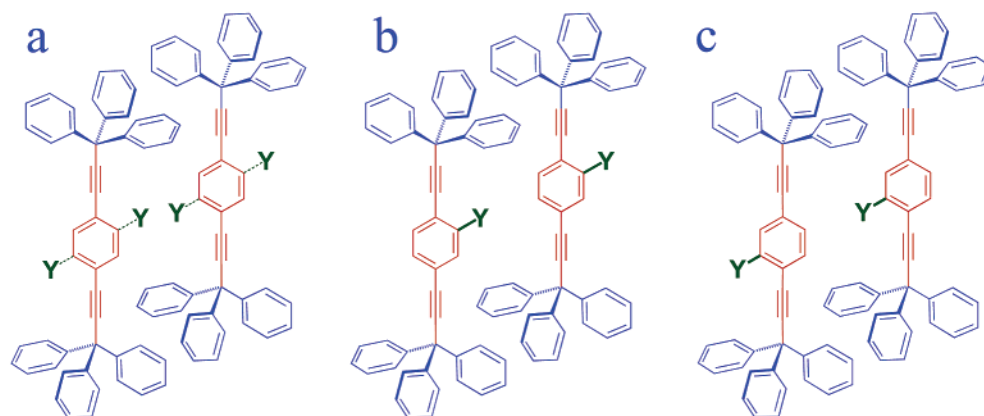
As it pertains to the dynamics of **1a–1e**, we previously showed that benzene-grown crystals of **1a** undergo a 2-fold phenylene flipping motion with a rate constant of $0.13 \times 10^3 \text{ s}^{-1}$ at 255 K and an estimated activation energy of 12.8 kcal/mol determined by variable temperature CPMAS ¹³C NMR.^{3,6} Solvent-free crystals of the same compound were shown to have a rate constant for rotation of $2.2 \times 10^6 \text{ s}^{-1}$ at 329 K and an activation barrier of 14.6 kcal/mol which were determined by variable temperature quadrupolar echo line-shape ²H NMR analysis. With that in mind, it is of interest to ask how the various polar groups in **1b–1e** may affect the rotational dynamics of their corresponding phenylenes. Although variable temperature CPMAS ¹³C NMR measurements in search of changes that could be assigned to dynamically exchanging

(24) Claborn, K.; Kahr, B.; Kaminsky, W. *CrystEngComm* **2002**, *4*, 252–256.

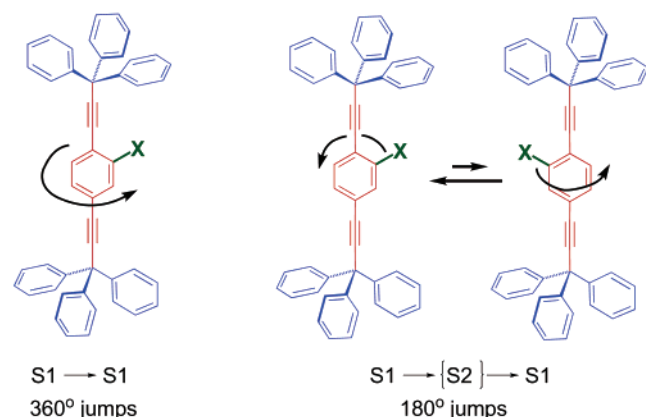
(25) Whitesell, J. K.; Davies, R. E.; Saunders, L. L.; Wilson, J. R.; Feagins, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 3267–3270.

(26) Gavezzotti, A. *J. Phys. Chem.* **1990**, *94*, 4319–4325.

Scheme 6



Scheme 7



nuclei²⁷ gave insufficient resolution to use the method, some qualitative insight on the possible dynamics of the polar phenylenes may be deduced from the crystallographic data. Noting that the disordered sites are related by a center of inversion, one may conclude that sites occupied by the polar groups ($Y = F, CN, NO_2, NH_2$) cannot be related by a dynamic process. A dynamic interconversion would require molecular rotation along the alkyne axis and inversion of the two axially chiral trityl groups in the solid state. A static disorder implies that, on average, a given molecule can have the polar group in either one of the two centrosymmetric sites (i.e., S1 in Scheme 7), but not on both. Under these constraints, rotation must be limited to (a) full 360° rotations ($S1 \rightarrow S1$) or (b) to two sequential 180° phenylene flips with the polar group having a very short residence time at the second site (S2) of a highly asymmetric rotational potential (i.e., $S1 \rightarrow S2 \rightarrow S1$). Dielectric spectroscopy and molecular modeling now in progress with the fluoro-derivative **1b** ($Y = F$) support the second mechanism and suggest the potential of variable temperature quadrupolar echo 2H NMR as an additional experimental technique to confirm this dynamic process.

3. Conclusions. Molecular compasses with trityl frameworks and polar phenylene rotors can be obtained in reasonable yields by Pd(0)-coupling reactions of 1,4-dibromophenylenes and tritylacetylene. Samples were prepared with fluoro (**1b**), cyano

(**1c**), nitro (**1d**), amino (**1e**), diamino (**1f**), and nitroamino (**1g**) substituents. While X-ray quality crystals of molecular compasses with two polar substituents (**1f** and **1g**) have not been obtained, samples of the monosubstituted compounds (**1b–1d**) crystallized from benzene gave rise to triclinic clathrate structures in the space group $P\bar{1}$ with two solvent molecules per unit cell, which can be desolvated by a first-order phase transition between 60 and 130 °C. The solvent-free structures obtained in this manner were shown to be spectroscopically and thermally identical to those obtained by crystallization from mixtures of CH_2Cl_2 and hexanes. Crystals of **1e** were only formed in the solvent-free $P\bar{1}$ modification and crystals of **1c** formed a third polymorph in the monoclinic space group $P2_1/c$. A detailed assignment of ^{13}C NMR signals in solution was used to assign the signals of the phenylene rotor in the solid state in an effort to determine whether variable temperature coalescence analysis may be used to determine the rates of gyroscopic motion in the solid state. Unfortunately, a strong spectral overlap between phenylene and trityl signals makes it impossible to apply this method. Nonetheless, ^{13}C CPMAS NMR spectra could be used to document the phase transitions between the various crystal forms which were also observed by DCS and TGA measurements. A qualitative analysis of the crystallographic data helped us formulate interesting questions regarding the formation of domains with locally aligned dipoles and the possible rotational dynamics of the central phenylene in terms of full rotations or sequential 2-fold flips along an asymmetric potential. Studies in progress to address these questions include the use of dielectric measurements as a function of frequency and temperature to determine the rates of dipolar motion in the solid state, molecular modeling, and the use of 2H NMR line-shape analyses.

Experimental Section

General. IR spectra were obtained on a Perkin-Elmer Paragon 100 FT-IR instrument. The 1H and ^{13}C NMR spectra were acquired on a Bruker NMR spectrometer at 500 and 125 MHz, respectively. The solvent used in all the cases was CD_2Cl_2 , with TMS as an internal standard. The DSC and TGA analyses were recorded on a Perkin-Elmer Pyris Diamond DSC and TG/DTA.

Materials. All the reagents and solvents were purchased from Aldrich, except 2,5-diiodofluorobenzene, the triethylamine and the copper (I) iodide, which were obtained from Matrix Scientific, Fisher, and Acros Organics, respectively. The chemicals were used without further purification, and triethylamine was deoxygenated by sparging with Ar for at least 2 h before to use.

(27) (a) Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208–216. (b) Horii, F.; Kaji, H.; Ishida, H.; Kuwabara, K.; Masuda, K.; Tai, T. *J. Mol. Struct.* **1998**, *441*, 303–311. (c) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Frydman, B.; Kustanovich, I.; Vega, S. *J. Am. Chem. Soc.* **1989**, *111*, 7001–7005.

2,5-Bis(3,3,3-triphenylpropynyl)fluorobenzene (1b). Bis(triphenylphosphine)palladium dichloride (0.024 g, 0.13 mmol), copper iodide (0.025 g, 0.13 mmol), triphenylphosphine (0.105 g, 0.4 mmol), and 2,5-diiodofluorobenzene (0.462 g, 1.3 mmol) were charged in a three-neck flask provided with a condenser and a magnetic stirrer. The flask was sparged with argon for 15 min after 30 mL of degassed triethylamine was added. The reaction mixture was heated in an oil bath to 85 °C and 3,3,3-triphenylpropyne (0.89 g, 3.32 mmol) previously dissolved in 20 mL of degassed triethylamine was added during a period of 1 h. The reaction mixture was heated an additional 18 h under argon. After cooling to room temperature, the reaction mixture was filtered and the triethylamine was evaporated. The product was purified by column chromatography (CH₂Cl₂:benzene:hexanes 1:1:8 by volume) to afford 0.19 g of (23%) **1b** as a white solid with moderate solubility. Analysis: mp = 270 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ 7.28 (m, 32 H, trityl unit and protons *ortho* and *para* to the F group), 7.46 (t, *J* = 7.6 Hz, 1H, *meta* to F). ¹³C NMR (125 MHz, CD₂Cl₂, TMS): δ 56.5, 56.8, 79.0, 84.3 (d, *J* = 3.0 Hz), 98.5, 102.6 (d, *J* = 3.5), 112.3 (d, *J* = 16.0 Hz), 118.7 (d, *J* = 22.9 Hz), 125.3 (d, *J* = 9.5 Hz), 127.3, 127.4, 127.7 (d, *J* = 3.5 Hz), 128.4, 128.5, 129.4, 129.5, 133.5 (d, *J* = 2.0 Hz), 145.2, 145.3, 162.9 (d, *J* = 250.8 Hz). IR (KBr): 3084, 3059, 3019, 2367, 2330, 2229, 1595, 1544, 1491, 1442, 1445, 1182, 1117, 1080, 1032, 1002, 874, 832, 754, 720, 698, 639 cm⁻¹. MS (70 eV): *m/z* (%) 628.2 (40, M⁺), 551.2 (13), 267.1 (100), 265.1 (55), 252.1 (30), 189.1 (19), 165.1 (72). HRMS (EI): calcd for C₄₈H₃₃F 628.2566; found 628.2562.

2,5-Bis(3,3,3-triphenylpropynyl)benzonitrile (1c). Molecular compass **1c** was obtained following the same procedure described above for compound **1b** in 10% isolated yield. Analysis: mp = 218 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ 7.31 (m, 30 H, trityl unit), 7.58 (d, *J* = 8.2 Hz, 1H, *meta* to CN), 7.67 (dd, *J* = 8.2, 1.5 Hz, 1H, *para* to CN), 7.80 (d, *J* = 1.5 Hz, 1H, *ortho* to CN). ¹³C NMR (125 MHz, CD₂Cl₂, TMS): δ 56.6, 56.9, 82.0, 83.4, 99.9, 103.9, 115.8, 117.5 (CN), 124.3, 126.7, 127.4, 127.5, 128.5, 129.4, 129.5, 132.9, 135.5, 135.9, 144.8, 145.0. IR (KBr): 3060, 3030, 2229, 1732, 1594, 1488, 1445, 1185, 1079, 1031, 1002, 908, 891, 842, 777, 758, 733, 662, 639 cm⁻¹. MS (70 eV): *m/z* (%) 635 (100, M⁺), 558 (18), 544 (10), 456 (6), 368 (8), 317 (10), 293 (27), 243 (24), 165 (165), 131 (70). HRMS (EI): calcd for C₄₉H₃₃N 635.2613; found 635.2596.

2,5-Bis(3,3,3-triphenylpropynyl)nitrobenzene (1d). Molecular compass **1d** was obtained following the same procedure described above for compound **1b** in 40.2% isolated yield. Analysis: mp = 229 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ 7.31 (m, 30 H, trityl unit), 7.65 (d, *J* = 8.2 Hz, 1H, *meta* to NO₂), 7.69 (dd, *J* = 8.2, 1.5 Hz, 1H, *para* to NO₂), 8.18 (d, *J* = 1.5 Hz, 1H, *ortho* to NO₂). ¹³C NMR (125 MHz, CD₂Cl₂, TMS): δ 56.6, 57.0, 80.9, 83.3, 100.1, 105.3, 118.5, 124.6, 127.4, 127.5, 127.8, 128.5, 128.6, 129.4, 129.5, 135.3, 135.8, 144.9, 145.0, 149.7. IR (KBr): 3054, 3030, 2322, 2231, 1599, 1540, 1519, 1504, 1487, 1445, 1360, 1261, 1180, 1079, 1031, 1002, 894, 838, 807, 780, 759, 733, 702, 659, 639 cm⁻¹. MS (70 eV): *m/z* (%) 655.2 (7, M⁺), 639.2 (17), 611.3 (53), 505.2 (34), 467.0 (17), 379.0 (63), 262.1 (45), 243.1 (36), 185.1 (79), 165.1 (100), 149.0 (26). HRMS (EI): calcd for C₄₈H₃₃NO₂ 655.2511; found 655.2498.

2,5-Bis(3,3,3-triphenylpropynyl)aniline (1e). Molecular compass **1e** was obtained following the same procedure described above for compound **1b** in 26% isolated yield. Analysis: mp = 284 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ 4.17 (s, 2H, NH₂), 6.84 (dd, *J* = 7.6, 1.5 Hz, 1H, *para* to NH₂), 6.86 (d, *J* = 0.9 Hz, 1H, *ortho* to NH₂), 7.30 (m, 31H, trityl unit and the hydrogens *meta* to NH₂). ¹³C NMR (125

MHz, CD₂Cl₂, TMS): δ 56.5, 56.9, 82.4, 85.8, 96.6, 102.7, 108.4, 117.1, 121.2, 124.5, 127.2, 127.3, 128.4, 128.5, 129.4, 129.5, 132.3, 145.5, 145.6, 148.6. IR (KBr): 3491, 3390, 3059, 3031, 2359, 2326, 2221, 1608, 1539, 1484, 1443, 1318, 1286, 1267, 1254, 1175, 1079, 1028, 816, 756, 697, 632 cm⁻¹. MS (70 eV): *m/z* (%) 625.3 (100, M⁺), 548.2 (30), 358.2 (26), 280.1 (15), 267.1 (14), 185.1 (23), 165.1 (20). HRMS (EI): calcd for C₄₈H₃₅N 625.2769; found 625.2755.

3,6-Bis(3,3,3-triphenylpropynyl)-1,2-phenylenediamine (1f). Molecular compass **1f** was obtained following the same procedure described above for compound **1b** in 22% isolated yield. Analysis: mp = 283 °C. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ 3.86 (s, 4 H, NH₂), 6.86 (s, 2H, spacer-phenyl), 7.30 (m, 30 H). ¹³C NMR (125 MHz, CD₂Cl₂, TMS): δ 56.88, 82.82, 102.2, 109.6, 122.1, 127.3, 128.5, 129.4, 136.9, 145.6. IR (KBr): 3418, 3340, 3062, 3027, 2353, 2327, 2219, 1616, 1598, 1445, 1207, 1180, 1072, 1031, 888, 803, 767, 752, 723, 697, 667, 637 cm⁻¹. MS (70 eV): *m/z* (%) 640.3 (100, M⁺), 563.3 (22), 454.1 (67), 373.2 (50), 295.1 (47), 243.1 (30), 185.1 (32), 182.0 (47), 165.1 (55). HRMS (EI): calcd for C₄₈H₃₆N₂ 640.2878; found 640.2875.

2,5-Bis(3,3,3-triphenylpropynyl)-4-nitroaniline (1g). Molecular compass **1g** was obtained in two steps. In the first of them was followed the same procedure described above for compound **1b**; however a mixture of molecular compass **1g** and 5-(3,3,3-triphenylpropynyl)-2-bromo-4-nitroaniline **2** (the product of a mono-coupling reaction) was obtained in a 1:3.5 proportion, then we added 1.5 equiv of 3,3,3-triphenyl-1-propyne to the mixture after a fast filtration by chromatographic column using as eluent the same mixture of solvent used before. The heating was continued until reaction completion (10 h); the total yield after purification in this case was 12.3%. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ 4.77 (s, 2H, NH₂), 6.88 (1, 1H, *ortho* to NH₂), 7.30 (m, 30 H, trityl unit), 8.25 (s, 1H, *ortho* to NO₂). ¹³C NMR (125 MHz, CD₂Cl₂, TMS): δ 56.9, 57.0, 80.1, 82.2, 103.6, 104.3, 107.6, 118.7, 121.1, 127.4, 127.5, 128.5, 128.6, 129.3, 129.5, 130.3, 139.3, 145.0, 145.1, 152.3. IR (KBr): 3486, 3384, 3058, 3027, 2221, 1614, 1538, 1514, 1506, 1488, 1445, 1312, 1256, 1183, 1100, 1032, 854, 757, 726, 697, 628 cm⁻¹. MS (70 eV): *m/z* (%) 670.3 (47, M⁺), 625.3 (20), 565.2 (20), 488.2 (16), 357.1 (18), 243.1 (19), 165.1 (37), 124.0 (100); 117.0 (79) HRMS (MALDI): calcd for C₄₈H₃₄N₂O₂ 670.2620; found 670.2623.

5-(3,3,3-triphenylpropynyl)-2-bromo-4-nitroaniline 2. ¹H NMR (500 MHz, CDCl₃, TMS): δ 4.57 (s, 2H, NH₂), 6.77 (1, 1H, *ortho* to NH₂), 7.26 (m, 18 H, trityl unit), 8.25 (s, 1H, *ortho* to NO₂). ¹³C NMR (125 MHz, CDCl₃, TMS): δ 56.6, 80.8, 103.4, 106.6, 118.9, 120.4, 127.0, 128.1, 129.2, 130.3, 139.3, 144.6, 148.4. IR (KBr): 3478, 3390, 3059, 3023, 2219, 1608, 1554, 1504, 1488, 1446, 1311, 1247, 1184, 1116, 1032, 891, 850, 755, 638 cm⁻¹.

Acknowledgment. This work was supported by NSF grants DMR9988439, CHE9871332 (X-ray), DMR9975975 (Solid State NMR), CHE9974928 (Avance 500 solution NMR) and DGE0114443 (IGERT). ZJD thanks CONACYT Mexico and the UC-Mexus program for a Postdoctoral Fellowship.

Supporting Information Available: Spectroscopic data ¹H and ¹³C NMR data of all compounds including HMBC spectra. X-ray diffraction data for **1b–1e** (CIF files) and packing diagram of **1e**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA035274B