Invisible but Common Motion in Organic Crystals: A Pedal Motion in Stilbenes and Azobenzenes

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Abstract: Some molecules that have a molecular skeleton similar to stilbenes and azobenzenes are known to show an orientational disorder in the crystals. Some of the disorders are known to be dynamic and mediated by a pedal motion in crystals. Dynamic processes of (*E*)-stilbene (**1**) and (*E*)-3,3′,4,4′-tetramethylazobenzene (**2**) in the crystals were investigated by X-ray diffraction analyses. The dynamic disorder and the pedal motion were detected at higher temperature, even in the molecules that showed no traces of the disorder at room temperature. The results demonstrated that the pedal motion should always be taken into account, even if no disorder is detected. The reasons for the nonoccurrence of the disorder and for the prevalence of the pedal motion are also discussed.

Introduction

The importance of molecular motion in crystals has increasingly been acknowledged for the past three decades, and extensive studies on this subject have been carried out in various areas of chemistry.[1] The information as to which types of molecular motion take place in crystals serves to explain the dynamic aspects of the molecules, such as reactivity, physical properties, and photochemical properties. The variety of molecular motion that is well-known to chemists and crystallographers is, however, extremely limited. Only a few types of molecular motion have systematically been studied: for example, the reorientation of the groups with approximate conical symmetry, such as methyl groups and *tert*-butyl groups;[2] the 2-fold reorientation of phenyl groups;[3] the in-plane reorientation of flat disklike molecules, such as benzene;[4] and the overall rotation of globular molecules, such as adamantane[5] and fullerene.[6] This paper reports on another molecular motion that is usually invisible and overlooked but commonly takes place in crystals.

In the crystal structures of stilbenes and azobenzenes, an orientational disorder (a misorientation of the molecules in the crystal lattice) was often observed (Figure 1).[7,8] At the disordered site, the molecules adopt the two conformations that are related by an approximate 2-fold rotation about the longest axis of the molecules.

Our recent study revealed that the disorder in some azobenzenes is dynamic and is ascribed to an interconversion between the two conformers in the crystals.[9] The conformational interconversion was inferred to take place through a pedal motion: a pair of benzene rings moves like the pedals of a bicycle (Figure 2).

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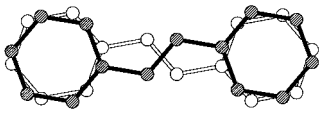


Figure 1. Orientational disorder for stilbenes and azobenzenes.

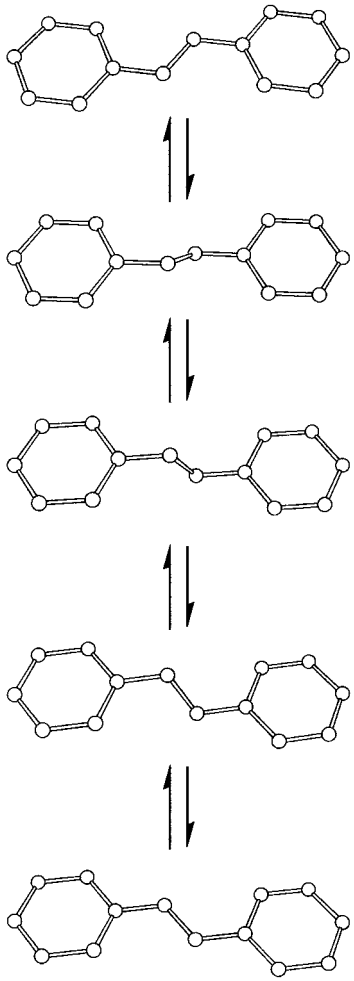
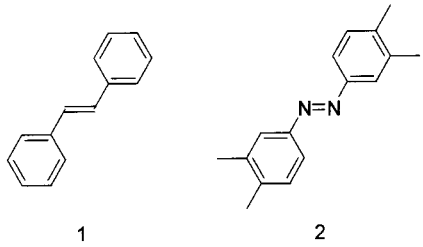


Figure 2. Pedal motion of stilbenes and azobenzenes.

Studies on the pedal motion of stilbenes and azobenzenes that used solid-state NMR spectroscopy,[10] measurements of heat capacity,[11] and molecular mechanics calculations[12] have been reported. A recent study on the photochromism of a salicylideneaniline revealed that the pedal motion is a key process of photoreaction in crystals.[13] Despite its importance, pedal motion has not been widely acknowledged and has been considered to occur only in the crystals that have an orientational disorder or a large void around the molecules, probably because it is difficult to detect and, therefore, easy to overlook. In this study, we carried out X-ray diffraction analyses of (*E*)-stilbene (**1**) and (*E*)-3,3′,4,4′-tetramethylazobenzene (**2**) at various temperatures. We will show that pedal motion takes place much more commonly than has been considered and should always be taken into account to understand the dynamic behavior of the molecules, even if no disorder is detected.



1 2

Experimental Section

Sample Preparation. Melting points were determined on a micro-hot-stage apparatus and were uncorrected. Compound **1** was purchased from Tokyo Kasei Co., and colorless crystals were obtained by recrystallization from methanol, mp 125.0−125.1 °C. Compound **2** was obtained by the reductive coupling[14] of 4-nitro-*o*-xylene, and red crystals were obtained by recrystallization from diethyl ether, mp 159.6−159.9 °C.

X-ray Diffraction Analysis. All of the diffraction measurements were carried out using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) ($2\theta_{max}$ = 55.0°). The temperature of the crystals was controlled using a Cryostream (Oxford Cryosystems) open-flow gas cryostat.[15] The temperature was held constant within ± 0.2 K during the measurement. About 2500 frames of data were collected for each data set using a narrow-frame method with scan widths of 0.3° in ω and 10 or 20 s exposure times. The frames were integrated with Bruker SAINT V6.02A. Unit cell parameters were determined by least-squares refinement of the three-dimensional centroids of several thousand reflections. The intensities were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied to the data using the SADABS program. No significant variation in the intensities before and after data collection was observed. The structure was solved by direct method with SHELXS-97.[16] Structures were refined by full-matrix least squares on F^2 using SHELXL-97.[17] For nondisordered molecules, all H atoms were located from difference Fourier maps and refined isotropically, and all C and N atoms were refined anisotropically. The crystal and experimental data are summarized in Table 1.

Results and Discussion

(*E*)-Stilbene (**1**) is one of the most well-known compounds that show the orientational disorder in crystals. The X-ray diffraction analyses of **1** have been reported many times by several groups over the past one-half century.[7,18] The structural features so far reported are as follows: There are two crystallographically independent molecules in the asymmetric unit (Figure 3). Both of the molecules lie at inversion centers and are almost planar. Molecules at one of the two crystal sites (referred to as site 1) have no disorder, and those at the other site (referred to as site 2) have the orientational disorder. The orientational disorder is dynamic, and the occupancy factor of the misoriented conformer decreases as the temperature is decreased.

We reinvestigated the crystal structures of **1** at various temperatures. Higher quality X-ray diffraction data obtained using a Bruker SMART 1000 CCD area detector enabled the disclosure of a dynamic disorder at site 1 that has long been

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Table 1. Crystal Data and Structure Refinements

compd	1					2	
emp form	$C_{14}H_{12}$					$C_{16}H_{18}N_2$	
form wt	180.24					238.32	
temp (K)	373	340	300	150	300 (before heating)	373	300 (after heating)
crystal system	monoclinic					triclinic	
space group	$P2_1/a$					$P\bar{1}$	
a (Å)	12.4420(8)	12.4056(7)	12.3803(6)	12.2995(6)	6.8119(7)	6.810(10)	6.8127(7)
b (Å)	5.7616(4)	5.7411(3)	5.7259(3)	5.6766(3)	7.1517(8)	7.207(11)	7.1529(7)
c (Å)	15.882(1)	15.7977(8)	15.7236(8)	15.5154(7)	7.6887(8)	7.793(12)	7.6903(8)
α (deg)	90.0	90.0	90.0	90.0	67.502(2)	67.39(3)	67.508(2)
β (deg)	111.810(1)	111.851(1)	111.895(1)	111.982(1)	74.118(2)	73.82(3)	74.153(2)
γ (deg)	90.0	90.0	90.0	90.0	79.837(2)	79.93(3)	79.857(2)
V (Å^3)	1057.0(1)	1044.3(1)	1034.22(9)	1004.52(9)	331.76(6)	338.1(9)	332.00(6)
Z	4					1	
reflections collected	13 415	13 312	13 161	12 606	4235	4328	4218
independent reflections	2429	2405	2383	2307	1522	1554	1520
R_{int}	0.017	0.016	0.016	0.012	0.008	0.011	0.009
data/restraints/parameters	2429/5/150	2405/5/150	2383/5/150	2307/5/150	1522/0/118	1554/0/118	1535/0/118
goodness-of-fit on F^2	1.086	1.078	1.103	1.097	1.044	1.068	1.056
$R[F^2 > 2\sigma(F^2)]$	0.051	0.049	0.047	0.040	0.049	0.056	0.048
$wR(F^2)$ (all data)	0.168	0.159	0.149	0.111	0.151	0.165	0.149
ρ_{min} (e Å^{-3})	−0.211	−0.238	−0.269	−0.291	−0.231	−0.227	−0.202
ρ_{max} (e Å^{-3})	0.215	0.220	0.237	0.313	0.191	0.180	0.190

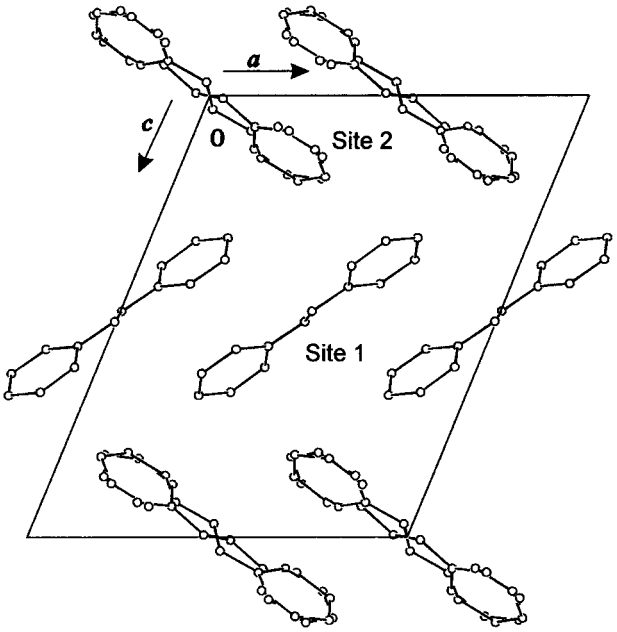

Figure 3. Projection of the crystal structure of (*E*)-stilbene (**1**) along the *b* axis, showing the disorder at site 2.

believed to be free from disorder.[7,19] Figure 4 shows the temperature dependence of the difference Fourier map at site 1. Each section contains four carbon atoms of the three central C−Ph and C═C bonds (C1, C7, C7′, and C1′). Two residual peaks (peaks A and A′) were found at room temperature (Figure 4b). The two peaks decreased in intensity as the temperature was decreased and disappeared at 150 K (Figure 4a). The height of the peaks increased as the temperature was raised, which is opposite the general tendency that density maps blur at higher temperatures (Figure 4c,d). The results clearly show that there is a dynamic disorder at site 1 and that the two peaks correspond to the ethylene carbon atoms (C7 and C7′) of the misoriented minor conformer. The temperature dependence of the Fourier map is ascribed to a change in the ratio of the two conformers as a function of the temperature. The change is mediated by the conformational interconversion through pedal motion. Thus, pedal motion takes place not only at site 2 but also at site 1 of the crystal of **1**.[20]

The results are consistent with the simulation using molecular mechanics packing energy calculations by Sironi and coworkers.[12] From the calculations they suggested that the failure to observe the disorder at site 1 is not attributable to unavailability of the pedal motion but to the large difference in the stability between the two conformers. The energy barrier for the pedal motion at site 1 was calculated to be 9.7 kcal mol^{-1}, which is not higher but, rather, is even lower than that at site 2 (15.1 kcal mol^{-1}). Thus, the motion at site 1 should be faster, not slower, than that at site 2. The difference in the energy of the two conformers at site 1 was calculated to be 2.6 kcal mol^{-1}, which is much larger than that at site 2 (0.7 kcal mol^{-1}). Thus, unfavorable Boltzmann's statistics assign only negligible population to the minor conformer at site 1.

The dynamic disorder and the pedal motion in the crystal of **1** have been overlooked despite repeated studies on the crystal structure. The fact that they are so difficult to detect suggests that they take place more generally than so far recognized and that most of them have been overlooked.

The crystal structure of 3,3′,4,4′-tetramethylazobenzene (**2**) should be another typical example that strongly supports this theory. X-ray diffraction analyses of **2** were carried out at various temperatures. Figure 5 shows the temperature dependence of the difference Fourier map of **2**. Each section contains two azo nitrogen atoms and two carbon atoms (C1, N1, N1′ and C1′). At 300 K, there were no residual peaks corresponding to the misoriented minor conformer (Figure 5a). At 373 K, two residual peaks (peaks A and A′) appeared around the N═N bond (Figure 5b). The two peaks can be obviously assigned to the nitrogen atoms of the misoriented minor conformer. After the diffraction measurement at 373 K, the same crystal was cooled to 300 K and the X-ray diffraction analysis was carried out. The difference Fourier map showed no residual peaks attributable to the minor conformer, like the map before heating (Figure 5c). This means that the occupancy factor of the minor conformer was reduced to being negligible. The results clearly

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(20) The ratio of the occupancy factors of two conformers at site 2 changed with variation of the temperature (80:20 at 373 K, 82:18 at 340 K, 85:15 at 300 K, and 94:6 at 150 K). The result confirms the dynamic nature of the disorder and the pedal motion at site 2.

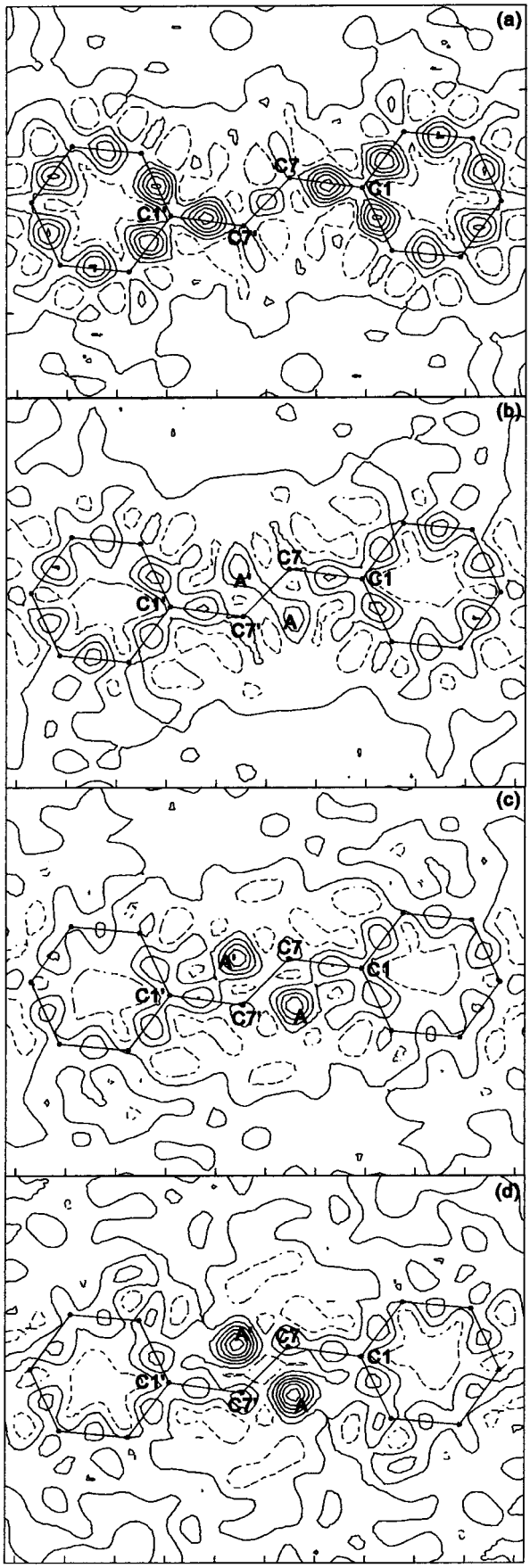

Figure 4. Difference Fourier maps of (*E*)-stilbene (**1**) at site 1. The section of each map contains C1, C7, C7′, and C1′. The contour lines are at 0.05 *e* Å^{-3} intervals. Negative contours are indicated by broken lines (a) at 150, (b) at 300, (c) at 340, and (d) at 373 K.

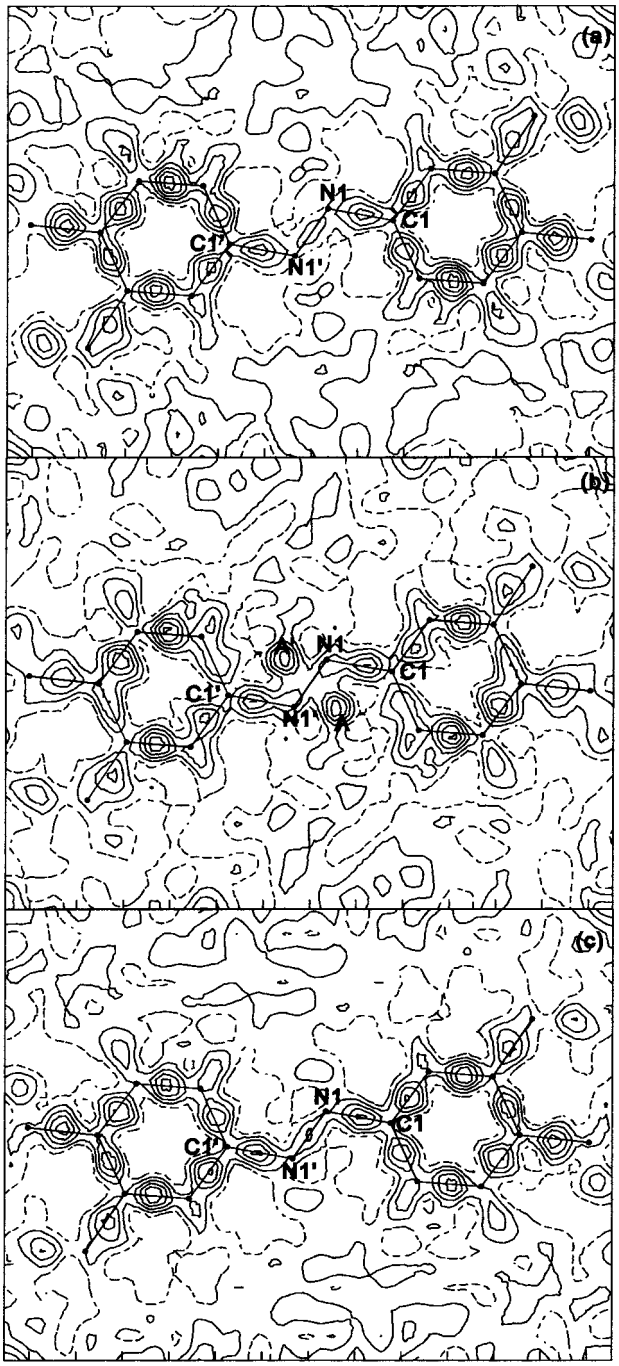

Figure 5. Difference Fourier maps of (*E*)-3,3′,4,4′-tetramethylazobenzene (**2**). The section of each map contains C1, N1, N1′ and C1′. The contour lines are at 0.05 *e* Å^{-3} intervals. Negative contours are indicated by broken lines (a) at 300 (before heating), (b) at 373, and (c) at 300 K (after heating).

show that there is a dynamic disorder due to the conformational interconversion through the pedal motion in the crystal of **2**. The occupancy factor of the minor conformer is too small to be detected at room temperature and becomes large enough to be detected at higher temperatures. The temperature dependence of the occupancy factor is reversible.

The above results suggest that the conformational interconversion through pedal motion takes place in most crystals of compounds that have a similar molecular skeleton, for example, stilbenes, azobenzenes, and benzylideneanilines. Most of them, however, were reported to be nondisordered.[21,22]

There are two possible explanations for the nonoccurrence of the disorder. The first one, which may be seemingly plausible, is based on an inhibition of the conformational interconversion as a result of a high-energy barrier to the pedal motion. If the activation energy of the pedal motion becomes very high in crystals, the rate of the conformational interconversion is greatly reduced. As a result, the occupancy factors of the conformers cannot obey the Boltzmann distribution law and only one conformer exists in the crystal. The other explanation is based on a low stability of the minor conformer. Even if the pedal motion takes place rapidly in crystals, a large difference in the stability between the two conformers greatly reduces the occupancy factor of the minor conformer.

In most crystals, the latter should be the determining factor for the following reasons. In molecules that have similar substituents at both ortho positions of a phenyl group, the major and minor conformers have almost equal stability in the gas phase. In molecules that have similar molecular skeletons, the pedal motion has a similar energy barrier and, thus, takes place at a similar frequency in the gas phase. Intermolecular interactions in crystals vary the relative stability of the two conformers and the energy barrier of the pedal motion. Destabilization of one conformer by only 2 kcal/mol reduces its occupancy factor to less than 4% at 300 K and makes the disorder difficult to detect.

To introduce an additional energy barrier that is enough to stop the pedal motion completely, much stronger intermolecular interactions are needed. In azobenzenes, for example, the pedal motion was reported to take place fairly fast, even in crystals (dozens of hertz at room temperature).[23,24] Introduction of an additional barrier as large as 7 kcal/mol can lengthen the correlation time to about an hour. Even with such conditions, a time that is much longer than an hour makes the conformers distribute according to the Boltzmann distribution law and gives rise to the disorder unless the minor conformer is strongly destabilized. The nonoccurrence of the disorder should then be mainly attributable to the destabilization of the minor conformer and does not mean that the pedal motion is inhibited. It is, therefore, highly probable that the pedal motion takes place even in nondisordered crystals.

Concluding Remarks

It is concluded that in the crystals of molecules that have a certain molecular skeleton, pedal motion takes place much more commonly than so far recognized. The low occupancy factor of the minor conformer makes the disorder invisible in most crystals. Irrespective of the detection of the disorder, pedal motion should always be taken into account when interpreting the dynamic properties of and gaining deeper insights into such crystals.

A recent study on a solid-state [2 + 2] photodimerization of *trans*-cinnamides[25] supports this suggestion. No disorder was detected in the crystal structures. The photoproducts, however, can be rationalized only when the pedal motion is assumed. In these crystals, the orientation of the "invisible" minor conformer is much more favorable for the dimerization than is the observed conformer. The reactivity of the crystals is, therefore, controlled by the "invisible" conformer. There should be more examples that can be rationalized on the assumption of pedal motion and the "invisible" conformer.

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Supporting Information Available: ORTEP diagrams for **1** and **2** (PDF); X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) In some such crystals, the reported geometrical parameters present some apparent anomalies, and the existence of unresolved disorder is strongly suspected. Some examples: (a) Gilardi, R. D.; Karle, I. L. *Acta Crystallogr. Sect. B* **1972**, *28*, 1635−1638. (b) Fitjer, L.; Wehle, D.; Noltemeyer, M.; Egert, E.; Sheldrick, G. M. *Chem. Ber.* **1984**, *117*, 203−221. (c) Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T.; Takamoto, M.; Wada, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 375−376.

(23) For 2′-acetamido-4′-[*N*,*N*-bis(2-methoxycarbonylethyl)amino]-4-nitroazobenzene, 45 Hz at 303 K.[10b]

(24) For 4,4′-dimethylazobenzene, 90 Hz at 306 K. Harada, J.; Ogawa, K.; Hayashi, S. Manuscript in preparation.

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