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Inner Rotation of the Exocyclic C=C Bonds of Methyl 2-Cyano-(2-methylcyclohepta[*b*]thiophen-8-ylidene)acetate and Methyl 2-Cyano-(1,2-dimethylcyclohepta[*b*]pyrrol-8-ylidene)acetate

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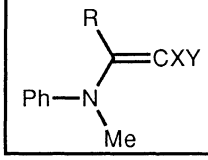
The rotational barrier of the exocyclic C=C bonds of heptafulvenes condensed with a hetero aromatic ring is dependent on electron donating ability of heterocycles and on the steric repulsion around the exocyclic C=C bond. The large negative entropies of activation are consistent with an extensively polarized transition state.

It has been demonstrated that some olefins carrying electron-withdrawing and electron-releasing groups, so-called push-pull ethylenes, isomerize thermally via an ionic transition state on the NMR time scale.[1-7]

As the study with **1** shows,[1] the rate of isomerization is sensitive to not only the nature of substituents but also the structural variations.



	$\Delta G^{\ddagger}$/kJmol^{-1}
1a: R=H, X=Y=COOMe	81.1(90°C)
1b: R=Me, X=Y=COOMe	41.8(-76.0°C)
1c: R=Me, X=COOMe, Y=CN	76.6(77°C)

The $\Delta G^{\ddagger}$ values of **1** are increased by the Me group and decreased by the CN group. The $\Delta S^{\ddagger}$ values were estimated from the magnitude of the difference in $\Delta G^{\ddagger}$ values; **1a**: -63 J·mol^{-1}K^{-1}, **1b**: 63-84 J·mol^{-1}K^{-1}, **1c**: -84 J·mol^{-1}K^{-1}.[1]

Herein, we report the effect of the hetero atoms (N, O, S) on the rotational process of heptafulvenes, which have greatly stabilized polar transition state.

The ^{1}H NMR spectrum of methyl 2-cyano-(2-methylcyclohepta[*b*]thiophen-8-ylidene)acetate (**2**)[8] showed a sharp doublet signal (J=12.1 Hz) at δ=8.46 and another (J=12 Hz) at 7.42 at -39.8 °C in CD_3CN solution, which were assigned to H-7. The ratio was 91/9. This implies the existence of two rotational isomers.
From a consideration of the magnetic anisotropy of a CO_2Me group, the one with a signal at 8.46 is assigned to be **2A** and the other is **2B**. In the major isomer **2A**, the smaller CN group is located at the inner side.

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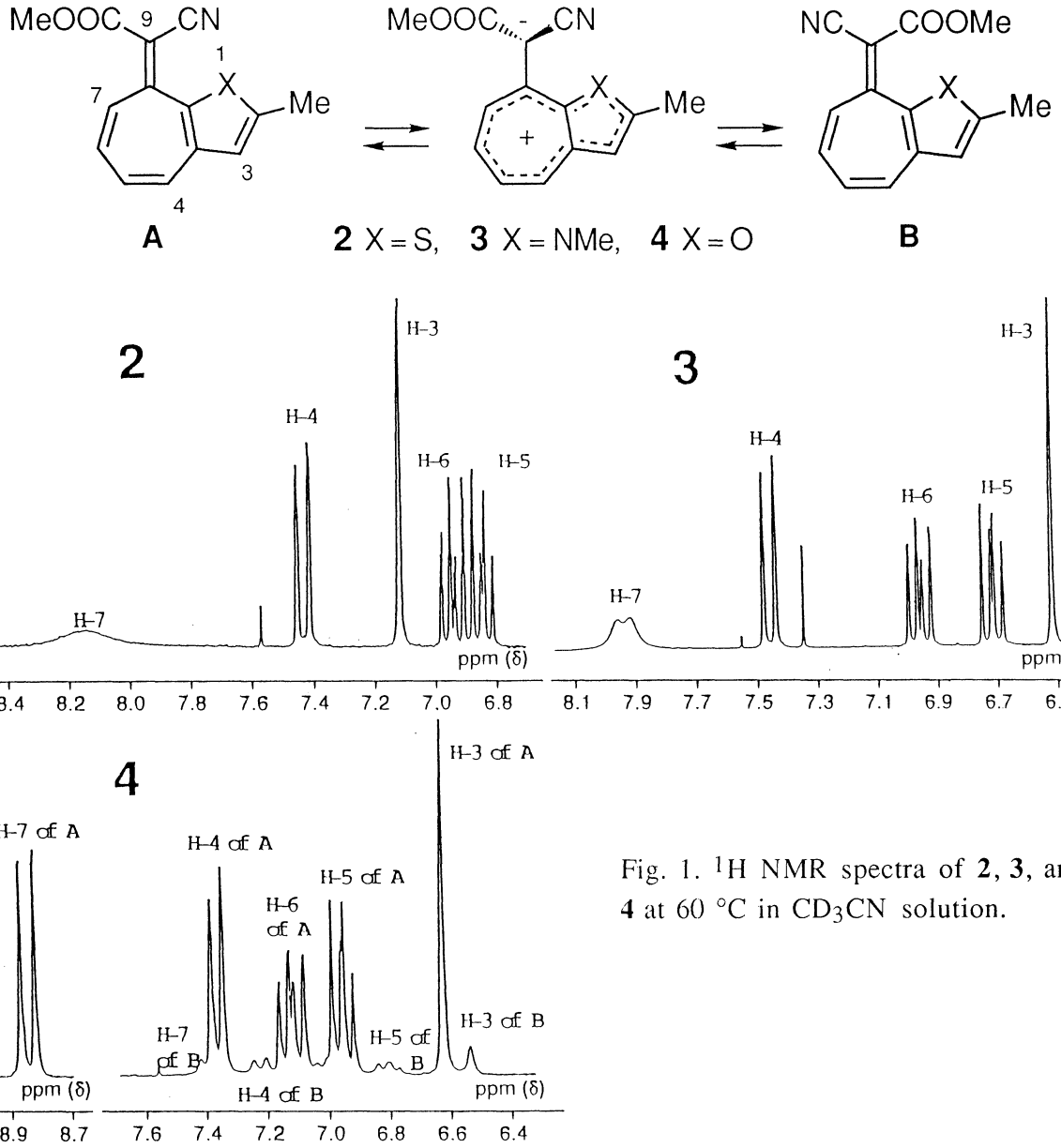

Fig. 1. ^{1}H NMR spectra of **2**, **3**, and **4** at 60 °C in CD_3CN solution.

In $CDCl_3$ solution at room temperature, the ^{1}H NMR spectrum of **2** showed a broad doublet signal (J=12 Hz) at δ 8.48, which was assigned to H-7 of **2A**. The doublet signal of another **2B**, however, was not observed. At 60 °C, the signal of H-7 was still a broad doublet at 8.40 (J=11.3 Hz) and did not coalesce in $CDCl_3$ solution. The signal of another isomer, **2B**, was undetectable. In CD_3CN solution at 60 °C, **2** showed a coalesced signal with a half-height of 46 Hz. The C=C bond, therefore, rotates faster in a polar solvent.

The ^{1}H NMR spectrum of methyl 2-cyano-(1,2-dimethylcyclohepta[*b*]pyrrol-8-ylidene)acetate (**3**)[8] showed broad signals at room temperature in CD_3CN solution. At -39.9 °C, it showed two rotational isomers **3A** (8.75, d, J=11.7 Hz, H-7) and **3B** (7.62,

d, J=12.1 Hz, H-7) with an inverse ratio, 30:70.[9] The bulkier CO_2Me group of the major isomer **3B** is located at an inner side of the molecule. At 60 °C, the broad doublet signal of H-7 appeared at 7.95.

On the other hand, the ^1H NMR spectrum of methyl 2-cyano-(1-methylcyclohepta[*b*]furan-8-ylidene)acetate (**4**)[8] in CD_3CN solution showed sharp signals of H-7 at δ 8.92 (d, J=12.8 Hz) and 7.42 (dd, J=12.8, 1.0 Hz) of two rotational isomers **4A** and **4B** in a ratio of 92:8 at 27 °C. At 60 °C, there still remained two doublets at 8.85 (J=12.8 Hz) and 7.23 (J=11.4 Hz). The rotation was prohibited under these conditions.

It is interesting to compare the configuration of the major isomer among **2**, **3**, and **4**. Since the trigonal CO_2Me group is bulkier than the linear CN group, **2A** and **4A**, in which the CO_2Me group is on the outer side of the molecule, are expected to be the dominating conformer on the steric ground. The major isomer **3B**, however, has a CO_2Me in the more hindered inner side of the molecule. The similar observation has been reported in methyl 2-cyano-3-dimethylamino-3-methylthioacrylate; the isomer, in which the CO_2Me and the NMe groups are cis, is dominating.[3]

The rotational barriers of **2** and **3** in CD_3CN solution were determined with the variable-temperature 270 MHz ^1H NMR spectra in the range of temperatures, -40 °C to 60 °C, and the complete line shape analysis by the simulation method.[10]

The activation parameters summarized in Table 1 show that the C=C bond of **3** rotates faster than those of **2** and **4**. The hetero atoms accelerate the rotation in the decreasing order N>S>O. A polar solvent enhances the rotation of **2**. These results imply that an ionic transition state such as a 10π system plays an important role.

Table 1. Activation parameters from the Eyring equation for the exchange between **A** and **B** in CD_3CN solution

	A / B	$\Delta H^{\ddagger}$/k·J·mol^{-1}	$\Delta S^{\ddagger}$/J·mol^{-1}K^{-1}	$\Delta G^{\ddagger}$/k·J·mol^{-1} at 298 K	r
2	91/9 at -39.8 °C	39.7±2.2	-77.9±8.0	62.9±4.6	0.9969
3	30/70 at -39.9 °C	39.5±1.0	-47.7±3.6	53.8±2.0	0.9995
4	92/8 at 27 °C	-	-	-	-

As shown in Table 1, the most significant difference in the activation parameters is the $\Delta S^{\ddagger}$ values; i.e., -78 J·mol^{-1}K^{-1} for **2** and -48 J·mol^{-1}K^{-1} for **3**. The $\Delta H^{\ddagger}$ values are essentially the same and the rates of rotation are apparently owing to the large negative $\Delta S^{\ddagger}$ term. The large negative $\Delta S^{\ddagger}$ values in a unimolecular reaction are interpreted to involve an extensively charge-separated transition state.[4,5] It is evident that **2** with large negative $\Delta S^{\ddagger}$ value has the more charge-separated transition state than **3**.

The ^{13}C NMR chemical shifts differences of the exocyclic C=C bond of heptafulvenes are δ 76.8 for **4**, 67.6 for **2** and 66.2 for **3**, which are in accord with the contri-

bution of the charge separation of the exocyclic C=C bond. The order is O>S>N. This implies that the O atom could conjugate better with a positive charge than the other hetero atoms if all other circumstances are equal.

While pyrrole is known to be a larger electron donor than furan and thiophene, the smallest chemical shift difference of **3** indicates that the donor capacity decreases due to the repulsion between the Me group on the N atom and the C8-C9 bond at the *peri*-position. Furthermore, this steric repulsion is expected to twist the C=C bond to increase the ground state energy and to make the rotational barrier of the C=C bond lower.[11] The order of the steric hindrance on the C=C bond is **3**>**2**>**4** (N>S>O), since a C-S bond length is longer than a C-O bond length.

Consequently, it is evident that the hetero atom affects the rate of the rotation in the decreasing order N>S>O. The Me group on the N atom in **3** decreases the contribution of the charge separation of the exocyclic C=C bond. Alternatively, the Me group on the N atom in **3** destabilizes the energy of the ground state to facilitate the isomerization. Both electronic and steric factors are concerned with the isomerization. From the chemical shift difference between the carbons of exocyclic C=C bond, it is concluded that furan is a better electron donor than pyrrole and thiophene.

Compound **4** should have the most polarized ground and transition states. The slow rate of **4**, being out of the NMR time scale, is attributable to the larger negative $\Delta S^{\ddagger}$ value and the more intensive solvation of the ground state than those of **2** and **3**.

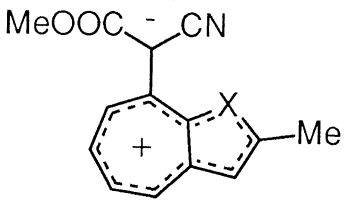

Fig. 2. Structure of the polarized ground state of heptafulvenes.

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8) Heptafulvenes were prepared from the corresponding tropones with methyl cyanoacetate in Ac_2O, which will be reported in the full paper.
9) The chemical shift of H-7 of (1,2-dimethylcyclohepta[*b*]pyrrol-8-ylidene)malononitrile is 7.43 (dm, J=12.0 Hz) in $CDCl_3$.
10) QCPE#140, G. Binsch and D. A. Kleier.
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