NMR studies on the axial chirality of *ortho*-substituted push–pull phenyl butadienes †

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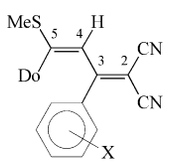
^{1}H NMR measurements of a series of *ortho*-phenyl substituted 3-aryl-2-cyano-5,5-bis(alkylthio)- (**3h**), 3-aryl-2-cyano-5-alkylthio-5-dialkylamino- (**4h**, **5**) and 3-aryl-2-cyano-5,5-bis(dialkylamino)penta-2,4-dienenitriles (**6**) with prochiral groups showed the rotation about the C-3–C-aryl bond to be hindered within the NMR timescale. The activation parameters of this atropisomerization process are discussed with respect to steric effects of substituents. The rotation barriers correlate with bond lengths and angles as determined by X-ray structure analyses.

Introduction

In our studies on intramolecular mobility of the push–pull butadienes **1** and **2** (Scheme 1) we observed slow rotations about



1 (Do = SMe), **2** (Do = NMe_2)
X = NMe_2, OMe, Me, H, Cl, Br, NO_2

Scheme 1

the C-2–C-3, C-3–C-4, C-4–C-5, and, for **2**, the C-5–N bonds.[1,2] Due to the π-electron interaction between the donor (Do) and acceptor groups and the diene double bond system these processes come into the NMR timescale and, therefore, are observable by dynamic NMR spectroscopy.

Furthermore, NMR spectra and X-ray crystal structure analyses[1–3] of **1** and **2** have established the twisting of the phenyl ring out of the plane of the butadiene chain pointing out significant steric interactions with the donor and acceptor groups. Therefore, suitable phenyl substitution should enhance the steric barrier to rotation about the C-3–C-aryl bond giving rise to atropisomers with a chirality axis along this bond. In the case of perpendicular arrangement of the phenyl ring and the butadiene chain an unsymmetrical substitution in the *ortho*- or *meta*-position is necessary, whereas for the torsion angle $\theta \neq 90°$, chirality would also appear at *para*- or unsubstituted compounds (Fig. 1).

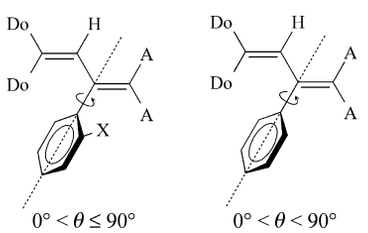
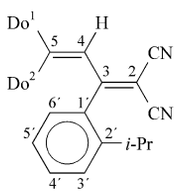


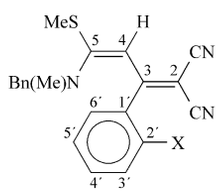
Fig. 1 Rotation about the C-3–C-aryl bond.

† Spectroscopic investigations on butadiene derivatives, Part 10. For Part 9, see ref. 1.

Referring to these considerations, the *ortho*-substituted push–pull butadienes **3**–**6** (Scheme 2) were prepared and studied



3h (Do^1 = Do^2 = SMe)
4h (Do^1 = SMe, Do^2 = NMe_2)
6h (Do^1 = Do^2 = $N(CH_2)_4$)



5a-g
5i (3-aryl = 3-(1naphthyl))

5	X
a	NMe_2
b	OMe
c	Me
d	H
e	Cl
f	Br
g	NO_2

Scheme 2

by dynamic ^{1}H NMR spectroscopy with respect to the stability of the chirality axis. With sufficiently high C-3–C-aryl rotation barriers, these compounds could be suitable precursors in asymmetric syntheses of heterocycles.[4]

The synthesis of axially chiral compounds is directly connected with the question of stability of the chirality axes. For preparative separation of isomers at room temperature, an energy barrier $\Delta G^{\neq}$ to rotation about the chirality axis of about 100 kJ mol^{-1} is necessary.[5] Since the activation parameters describe the energy difference between ground states (GS) and transition states (TS), to enhance the barrier to C-3–C-aryl rotation, for instance by *ortho*-substitution, the influence of substituents on the GS as well as the TS has to be considered. A sterically bulky substituent does not inevitably lead to an increased energy barrier.[6] In the case of strong electron-donating or -withdrawing groups electronic effects are of importance.[7]

Concerning the rotation about the C-3–C-aryl bond in **3**–**6**, it was confirmed that the molecule is twisted in the GS similar to biphenyl derivatives.[8] The phenyl ring is twisted out of the butadiene plane and, therefore, steric interactions with the substituent X in the GS should be of minor importance. The TS is supposed to be a nearly planar arrangement of the phenyl ring with the plane of the atoms C-2–C-3–C-4, whereas the remaining butadiene structure is twisted. In accordance with the rotation barriers found for the butadiene chain,[2b] the twisting of the donor part about the C-3–C-4 single bond should

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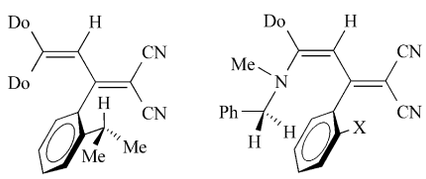
Table 1 Activation parameters of the C-3–C-aryl rotation of butadienes **3**–**6** (0.05 M; r_V = van der Waals radius[8,15,16])

	X	r_V/Å	Solvent	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}_{303K}$/kJ mol^{-1}
3h	*i*-Pr	1.96	$CDCl_3$	69.3 ± 0.6	2 ± 2	68.6 ± 0.2
4h	*i*-Pr	1.96	$CDBr_3$	73.3 ± 0.5	−11 ± 1	76.6 ± 0.3
6h	*i*-Pr	1.96	$CDBr_3$	67.1 ± 1.0	−30 ± 3	76.2 ± 0.4
5a	NMe_2	1.63		—	—	61.8 ± 0.2
5b	OMe	1.52	CD_2Cl_2	44.4 ± 1.1	−31 ± 4	53.8 ± 0.4
5c	Me	1.72	$CDCl_3$	58.3 ± 0.5	−22 ± 2	64.9 ± 0.2
5e	Cl	1.75	$CDCl_3$	60.9 ± 0.6	−16 ± 2	65.8 ± 0.2
5f	Br	1.85	$CDCl_3$	—	—	70.0 ± 0.3
			$CDBr_3$	65.7 ± 0.4	−12 ± 1	69.3 ± 0.2
5g	NO_2	1.79	$CDCl_3$	63.6 ± 0.5	−12 ± 2	67.2 ± 0.2
5i	—	—	$CDBr_3$	69.3 ± 0.5	−9 ± 1	72.1 ± 0.3

proceed more easily than the twisting of the nitrile groups about the C-2–C-3 double bond. Consequently, the rotation about the C-3–C-aryl bond would be characterized by two transition states, but, in the energy-lower state of the butadienes **3**–**6**, the *ortho*-substituent will be moved about the more flexible donor side. These considerations are in agreement with results of quantum chemical calculations (see below). By dynamic NMR measurements this rotation process can only be observed if the enantiotopy and diastereotopy, respectively, of substituents of prochiral groups are changed (Scheme 3).[9]



Scheme 3

With that, exclusively the energy-lower step of the C-3–C-aryl rotation is detectable. Due to the planar transition state steric interactions cause higher TS energies and, therefore, increasing size of X should lead to higher rotation barriers.

Experimental

The ^{1}H and ^{13}C NMR measurements of 0.05 M solutions of **3**–**6** were performed on a Bruker ARX-300 spectrometer at 300.1 MHz and 75.5 MHz, respectively. The halogen containing solvents given in Table 1 were dried over molecular sieves or sodium sulfate and purified with basic aluminium oxide to remove acid impurities. For low-temperature measurements, argon was bubbled through the solution to remove impurities of paramagnetic oxygen. The probe temperature was measured by means of thermometer liquids.[10] The exchange rates and activation parameters were obtained by CLSA (Complete Line Shape Analysis) of the prochiral groups *i*-Pr or Bn (Scheme 3) using the program DNMR5.[11] The errors given in this paper refer to statistical errors of the linear regression $\Delta G^{\neq}$ *vs.* T in limits of 95% reliability (see ref. 12), for $\Delta G^{\neq}_{303K}$ including a systematic temperature error of about ± 1 K. The real errors on $\Delta H^{\neq}$ and $\Delta S^{\neq}$ might be much larger. The true errors on $\Delta G^{\neq}_{303K}$ approach the fitting errors, because the significant line-form alterations used for CLSA are in a relatively small range near room temperature and, therefore, the errors in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ concerning the calculation of $\Delta G^{\neq}_{303K}$ should to be neglected.

The X-ray diffraction results were obtained on a Bruker P4 four circle diffractometer with λ(Mo-K$_\alpha$) = 0.71073 Å with graphite monochromator. After taking rotational photos and determining reasonable reduced cells a data collection was started in routine ω-scan. The structures were solved with direct methods (Bruker SHELXTL) and refined with the full-matrix least-squares method of SHELXL-97.[13] All non-hydrogen atoms were refined anisotropically whereas the hydrogens were put into theoretical positions and refined according to the riding model.

The synthesis of butadienes **3h** and **4h** is described in ref. 1. The butadienes **5** were prepared according to ref. 1, **6h** according to ref. 14. For all compounds, the experimental values of elemental analyses correspond to the calculated values within acceptable errors.

Synthesis of 3-aryl-5-benzyl(methyl)amino-2-cyano-5-methylthiopenta-2,4-dienenitriles (5) (general procedure)

2 mmol of the butadiene **3** in 8 mL of *N*-benzylmethylamine were stirred for 1–3 h at 100 °C. After cooling and addition of 10 mL of $CHCl_3$ and water the reaction mixture was shaken with 2 mL (20 mmol) of conc. HCl, the organic phase was separated, washed three times with 10 mL of water and dried over Na_2SO_4. The $CHCl_3$ was distilled off, the residue oil was dissolved in a small amount of EtOH and, after crystallization, recrystallized from EtOH.

5-Benzyl(methyl)amino-2-cyano-3-(2-dimethylaminophenyl)-5-methylthiopenta-2,4-dienenitrile (5a). Yield: 56%, red crystals, mp 139–141 °C (EtOH). ^{1}H NMR: δ (ppm) = 2.16 (s, 3H, SCH_3), 2.76 (s, 6H, NCH_3), 2.93 (s, 3H, NCH_3), 4.56 (br, 2H, NCH_2), 5.74 (s, 1H, H-4), 6.96 (m, 1H, H-5′), 6.97 (m, 1H, H-3′), 7.12 (m, 2H, *o*-Bn), 7.17 (m, 1H, H-6′), 7.32 (m, 1H, *p*-Bn), 7.33 (m, 1H, H-4′), 7.36 (m, 1H, *m*-Bn). ^{13}C NMR: δ (ppm) = 18.5 (SCH_3), 40.4 (NCH_3), 43.3 (NCH_3), 58.8 (NCH_2), 66.4 (C-2), 99.2 (C-4), 117.1 (CN), 117.3 (CN), 117.7 (C-3′), 120.8 (C-5′), 127.4 (*o*-Bn), 128.2 (*p*-Bn), 128.4 (C-1′), 129.0 (*m*-Bn), 131.0 (C-4′), 131.1 (C-6′), 135.3 (*i*-Bn), 151.3 (C-2′), 169.6 (C-3), 170.0 (C-5). MS (70 eV): m/z = 388 (M^+).

5-Benzyl(methyl)amino-2-cyano-3-(2-methoxyphenyl)-5-methylthiopenta-2,4-dienenitrile (5b). Yield: 75%, yellow–orange crystals, mp 140–141 °C (EtOH). ^{1}H NMR: δ (ppm) = 2.18 (s, 3H, SCH_3), 2.94 (s, 3H, NCH_3), 3.84 (s, 3H, OCH_3), 4.60 (br, 2H, NCH_2), 5.76 (s, 1H, H-4), 6.94 (m, 1H, H-3′), 6.96 (m, 1H, H-5′), 7.10 (m, 2H, *o*-Bn), 7.11 (m, 1H, H-6′), 7.30 (m, 1H, *p*-Bn), 7.34 (m, 2H, *m*-Bn), 7.38 (m, 1H, H-4′). ^{13}C NMR: δ (ppm) = 18.4 (SCH_3), 40.7 (NCH_3), 55.6 (OCH_3), 58.7 (NCH_2), 68.0 (C-2), 101.0 (C-4), 111.4 (C-3′), 116.8 (CN), 117.0 (CN), 120.5 (C-5′), 126.2 (C-1′), 127.4 (*o*-Bn), 128.2 (*p*-Bn), 129.0 (*m*-Bn), 129.9 (C-6′), 131.4 (C-4′), 135.3 (*i*-Bn), 156.8 (C-2′), 166.8 (C-3), 169.6 (C-5). MS (70 eV): m/z = 375 (M^+).

5-Benzyl(methyl)amino-2-cyano-3-(2-methylphenyl)-5-methylthiopenta-2,4-dienenitrile (5c). Yield: 64%, orange crystals, mp 83–87 °C (EtOH). ^{1}H NMR: δ (ppm) = 2.01 (s, 3H, SCH_3), 2.31 (CH_3), 3.01 (s, 3H, NCH_3), 4.62, 4.74 (2 × br, 2H, NCH_2), 5.89 (s, 1H, H-4), 7.06 (m, 1H, H-6′), 7.13 (m, 2H, *o*-Bn), 7.19 (m, 1H, H-5′), 7.22 (m, 1H, H-3′), 7.28 (m, 1H, H-4′), 7.36 (m, 3H, *m*-Bn, *p*-Bn). ^{13}C NMR: δ (ppm) = 18.2 (SCH_3), 19.8 (CH_3), 40.6 (NCH_3), 58.4 (NCH_2), 69.4 (C-2), 102.7 (C-4), 116.1 (CN), 116.2 (CN), 125.6 (C-5′), 127.4 (*o*-Bn), 128.3 (*p*-Bn), 128.3 (C-6′), 129.1 (*m*-Bn), 129.4 (C-4′), 130.5 (C-3′), 135.1 (*i*-Bn),

136.0 (C-2′), 137.1 (C-1′), 167.5 (C-5), 170.4 (C-3). MS (70 eV): m/z = 359 (M^+).

5-Benzyl(methyl)amino-2-cyano-5-methylthio-3-phenylpenta-2,4-dienenitrile (5d). Yield: 65%, orange crystals, mp 137–138 °C (EtOH). ^{1}H NMR: δ (ppm) = 2.28 (s, 3H, SCH_3), 2.92 (s, 3H, NCH_3), 4.60 (s, 2H, NCH_2), 5.56 (s, 1H, H-4), 7.12 (m, 2H, *o*-Bn), 7.29–7.49 (m, 8H, H-2′,3′,4′, *m*-Bn, *p*-Bn). ^{13}C NMR: δ (ppm) = 18.7 (SCH_3), 41.0 (NCH_3), 58.8 (NCH_2), 65.2 (C-2), 99.1 (C-4), 117.0 (CN), 117.2 (CN), 127.5 (*o*-Bn), 128.3 (*p*-Bn), 128.4 (C-3′), 129.1 (*m*-Bn), 129.3 (C-2′), 130.8 (C-4′), 135.0 (*i*-Bn), 137.0 (C-1′), 169.6 (C-3), 171.9 (C-5). MS (70 eV): m/z = 345 (M^+).

5-Benzyl(methyl)amino-3-(2-chlorophenyl)-2-cyano-5-methylthiopenta-2,4-dienenitrile (5e). Yield: 62%, orange crystals, mp 88–93 °C (EtOH). ^{1}H NMR: δ (ppm) = 2.08 (s, 3H, SCH_3), 3.05 (s, 3H, NCH_3), 4.70, 4.77 (2 × br, 2H, NCH_2), 5.87 (s, 1H, H-4), 7.15 (m, 2H, *o*-Bn), 7.28 (m, 1H, H-6′), 7.31 (m, 2H, H-4′, H-5′), 7.34 (m, 1H, *p*-Bn), 7.36 (m, 2H, *m*-Bn), 7.42 (m, 1H, H-3′). ^{13}C NMR: δ (ppm) = 18.6 (SCH_3), 40.6 (NCH_3), 58.6 (NCH_2), 69.0 (C-2), 102.0 (C-4), 116.0 (2 × CN), 126.8 (C-5′), 127.4 (*o*-Bn), 128.4 (*p*-Bn), 129.1 (*m*-Bn), 130.0 (C-3′), 130.5 (C-6′), 130.7 (C-4′), 132.5 (C-2′), 135.0 (*i*-Bn), 136.2 (C-1′), 166.6 (C-3), 168.0 (C-5). MS (70 eV): m/z = 379 (M^+).

5-Benzyl(methyl)amino-3-(2-bromophenyl)-2-cyano-5-methylthiopenta-2,4-dienenitrile (5f). Yield: 68%, orange crystals, mp 104–108 °C (EtOH). ^{1}H NMR: δ (ppm) = 2.07 (s, 3H, SCH_3), 3.06 (s, 3H, NCH_3), 4.70, 4.80 (2 × d, 2H, NCH_2, J = 14.9 Hz), 5.88 (s, 1H, H-4), 7.16 (m, 2H, *o*-Bn), 7.26 (m, 1H, H-4′), 7.27 (m, 1H, H-6′), 7.33 (m, 1H, *p*-Bn), 7.35 (m, 1H, H-5′), 7.37 (m, 2H, *m*-Bn), 7.61 (m, 1H, H-3′). ^{13}C NMR: δ (ppm) = 18.6 (SCH_3), 40.5 (NCH_3), 58.5 (NCH_2), 69.1 (C-2), 102.3 (C-4), 116.0 (2 × CN), 122.1 (C-2′), 127.3 (C-5′), 127.5 (*o*-Bn), 128.4 (*p*-Bn), 129.1 (*m*-Bn), 130.6 (C-6′), 130.7 (C-4′), 133.2 (C-3′), 135.0 (*i*-Bn), 138.2 (C-1′), 167.5 (C-5), 168.0 (C-3). MS (70 eV): m/z = 423 (M^+).

5-Benzyl(methyl)amino-2-cyano-5-methylthio-3-(2-nitrophenyl)penta-2,4-dienenitrile (5g). Yield: 72%, yellow–orange crystals, mp 115–118 °C (EtOH). ^{1}H NMR: δ (ppm) = 1.97 (s, 3H, SCH_3), 3.03 (s, 3H, NCH_3), 4.66, 4.74 (2 × d, 2H, NCH_2, J = 15.0 Hz), 5.89 (s, 1H, H-4), 7.14 (m, 2H, *o*-Bn), 7.33 (m, 1H, *p*-Bn), 7.37 (m, 2H, *m*-Bn), 7.42 (m, 1H, H-6′), 7.59 (m, 1H, H-4′), 7.69 (m, 1H, H-5′), 8.06 (m, 1H, H-3′). ^{13}C NMR: δ (ppm) = 18.7 (SCH_3), 40.4 (NCH_3), 58.4 (NCH_2), 69.2 (C-2), 102.5 (C-4), 115.4 (CN), 115.6 (CN), 124.7 (C-3′), 127.4 (*o*-Bn), 128.4 (*p*-Bn), 129.2 (*m*-Bn), 130.5 (C-4′), 131.1 (C-6′), 132.8 (C-1′), 133.2 (C-5′), 134.8 (*i*-Bn), 148.3 (C-2′), 166.1 (C-5), 166.3 (C-3). MS (70 eV): m/z = 390 (M^+).

5-Benzyl(methyl)amino-2-cyano-5-methylthio-3-(1-naphthyl)-penta-2,4-dienenitrile (5i). Yield: 72%, yellow crystals, mp 155–156 °C (EtOH). ^{1}H NMR: δ (ppm) = 1.66 (s, 3H, SCH_3), 2.98 (s, 3H, NCH_3), 4.54, 4.69 (2 × d, 2H, NCH_2, J = 15.0 Hz), 6.14 (s, 1H, H-4), 7.06 (m, 2H, *o*-Bn), 7.28–7.39 (m, 3H, *m*-Bn, *p*-Bn), 7.41–7.52 (m, 4H, H-2′-,3′-,6′-,7′-Naph), 7.75–7.79 (m, 1H, H-8′-Naph), 7.85–7.91 (m, 2H, H-4′-,5′-Naph). ^{13}C NMR: δ (ppm) = 18.3 (SCH_3), 40.6 (NCH_3), 58.4 (NCH_2), 69.9 (C-2), 103.3 (C-4), 116.2 (CN), 116.3 (CN), 124.7 C-8′-Naph), 125.1 (C-2′-Naph), 126.2 (C-6′-Naph), 126.6 (C-3′-Naph), 127.0 (C-7′-Naph), 127.4 (*o*-Bn), 128.3 (*p*-Bn), 128.6 (C-5′-Naph), 129.1 (*m*-Bn), 130.1 (C-4′-Naph), 131.2 (C-9′-Naph), 133.5 (C-10′-Naph), 134.8 (C-1′-Naph), 135.0 (*i*-Bn), 167.5 (C-5), 168.9 (C-3). MS (70 eV): m/z = 395 (M^+).

Synthesis of 2-cyano-3-(2-isopropylphenyl)-5,5-dipyrrolidinopenta-2,4-dienenitrile (6h)

1.5 mmol of **3h** in 2 mL of pyrrolidine were refluxed for 2 h under stirring. After removing the solvent and dissolution in a little EtOH the formed crystals were recrystallized from EtOH. Yield: 55%, yellow–green needles, mp 203–204 °C. ^{1}H NMR: δ (ppm) = 1.17 (d, 3H, CHCH_3, J = 6.9 Hz), 1.34 (d, 3H, CHCH_3, J = 6.8 Hz), 2.06 (br, 4H, CH_2-3″), 3.26 (m, 1H, CHCH$_3$), 3.62 (br, 4H, NCH_2), 4.44 (s, 1H, H-4, s-*cis*-conformer (95%)), 5.26 (s, 1H, H-4, s-*trans*-conformer (5%)), 7.01 (m, 1H, H-6′), 7.12 (m, 1H, H-5′), 7.32 (m, 1H, H-4′), 7.35 (m, 1H, H-3′). ^{13}C NMR: δ (ppm) = 23.5, 25.3 (CHCH$_3$), 26.0 (CH_2-3″), 29.0 (CHCH$_3$), 45.8 (C-2), 50.9 (NCH_2), 94.2 (C-4), 121.0 (CN), 125.4 (C-5′), 125.5 (C-3′), 128.1 (C-6′), 128.7 (C-4′), 139.1 (C-1′), 145.9 (C-2′), 160.4, 160.8 (C-3,5). MS (70 eV): m/z = 360 (M^+).

Results and discussion

The NMR detection of chirality was performed using prochiral isopropyl and benzyl groups. The methyl groups of the isopropyl moiety in **3h**, **4h** and **6h** are nonequivalent at room temperature and show line-shape alterations on increasing the temperature. The CH_2 signal of the benzyl group shows different line-shapes at room temperature depending on bulkiness of the *ortho*-phenyl substituents, *e.g.* unequivocal AB spectra for **5f**, **i** and time-averaged signals for **5a**, **b**. Examples for line-shape alterations of the isopropyl and benzyl signals are given in Fig. 2 and Fig. 3. In addition, rotations about the butadiene bonds could also be observed.[1]

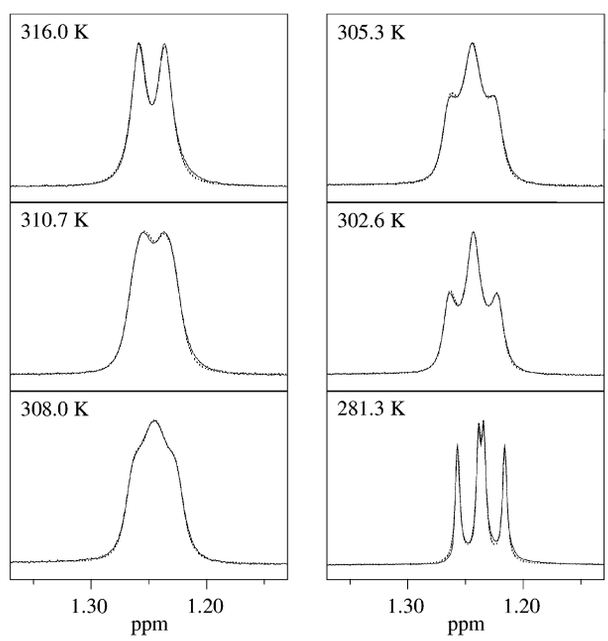


Fig. 2 Temperature-dependent experimental and calculated (dotted lines) ^{1}H NMR spectra of **3h** (expanded plot of CH-*Me* signals).

C-3–C-aryl rotation barriers of butadienes 3h, 4h and 6h

The dependence of the C-3–C-aryl rotation barrier on substituents of the butadiene chain was studied for **3h**, **4h** and **6h** (X = *i*-Pr in each case) (Table 1). As can be seen from $\Delta G^{\neq}_{303K}$, no compound possesses a stable chirality axis at room temperature. The significant increase **3h** ⟶ **4h** of about 8 kJ mol^{-1} on substitution of a methylthio by a dimethylamino group is due to the stronger donor effect of the amino group. It stabilizes the GS of the C-3–C-aryl bond in **4h** by conjugative interactions, whereas it should not play a role in the TS owing to torsion of the donor part.

The lack of a further increase in the rotation barrier on going from **4h** to **6h** can be explained by the different conformational structure of the butadiene chain. NMR chemical shifts and X-ray data prove the s-*trans* conformation for the butadienes **3h**

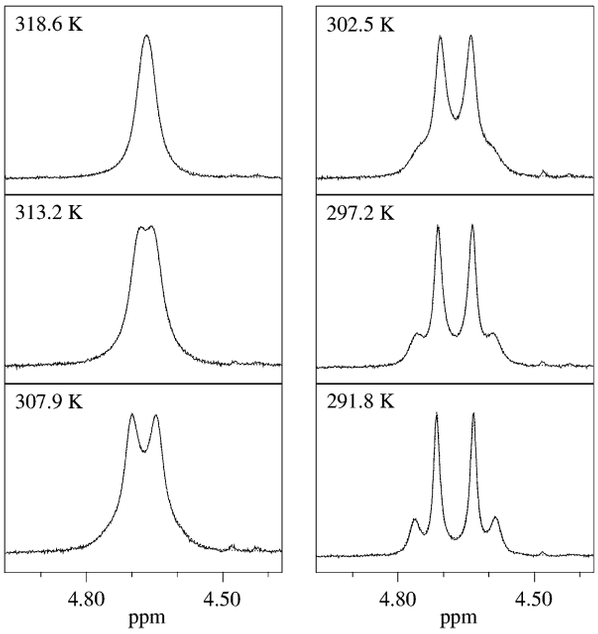


Fig. 3 Temperature-dependent experimental and calculated (dotted lines) ^{1}H NMR spectra of **5c** (expanded plot of CH_2 signal).

and **4h** at room temperature, whereas for **6h** the s-*cis* conformation was found to be favoured (see below).

In the GS the twisted phenyl ring in both conformations should exhibit comparable steric interactions with the donor as well as acceptor groups. In the planar TS, the phenyl group in the s-*cis* butadiene has a greater mobility because the steric interactions with the donor side are omitted. This effect could lead to a decrease of the rotation barrier and compensate the donor stabilizing of the ground state discussed above.

C-3–C-aryl rotation barriers of compounds 5

The influence of different *ortho*-phenyl substituents X on the C-3–C-aryl rotation has been studied for the monoaminobutadienes **5a**–**g** including, in addition, the naphthyl-substituted compound **5i** (Table 1).

In the case of **5a** the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were not obtainable with sufficient accuracy because of additional line-broadening at low temperatures. For **5f** in chloroform solution, the temperature range for the analysis was limited by the low boiling point of the solvent, therefore, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are not given. However, since line-shape alterations of the benzyl signals at room temperature could be observed and calculated for both compounds, the $\Delta G^{\neq}_{303K}$ values are correct as given for the other butadienes **5** (Table 1).

For the unsubstituted compound **5d**, activation parameters have not been determined due to further rotation processes and line-broadening in the temperature range concerned. Therefore, the assignment and determination of spectral parameters were impossible. However, the C-3–C-phenyl rotation is not necessarily observed ($\theta = 90°$, Fig. 1).

The $\Delta G^{\neq}_{303K}$ values of butadienes **5b**–**g** are ranged corresponding to the size of substituents. A linear correlation between $\Delta G^{\neq}_{303K}$ and van der Waals radii r_V of the *ortho*-substituents X including **4h** (Table 1, **5f** in $CDCl_3$) was found (Fig. 4, eqn. (1)).

The atom radii of chlorine, bromine and oxygen[15] (equal to methoxy group)[8] and effective radii of the methyl, nitro and isopropyl group[16] were included into the correlation. From the close correlation it can be concluded that the height of energy barriers of the C-3–C-aryl rotation is exclusively attributed to steric effects.

Compound **5a** (X = NMe_2) has not been included. The $\Delta G^{\neq}_{303K}$ value of the C-3–C-aryl rotation is about 2 kJ mol^{-1} above the regression line. The deviation can be explained by the

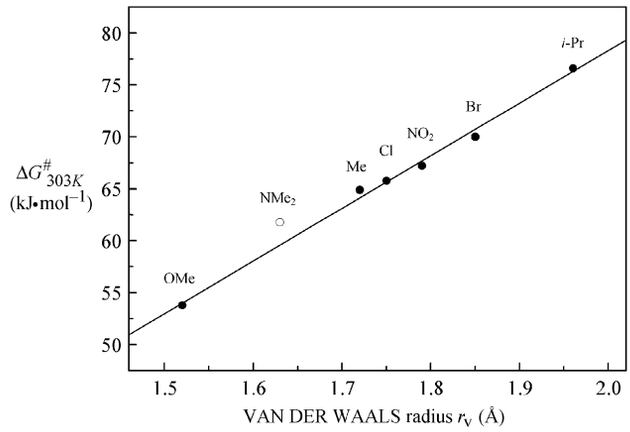
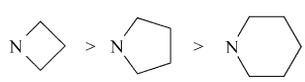


Fig. 4 Correlation of $\Delta G^{\neq}_{303K}$ of C-3–C-aryl rotation of the butadienes **5a**–**g** (**5f** in $CDCl_3$) and **4h** with the van der Waals radii of the *ortho*-substituent X (○ not included (see text)).

$$\Delta G^{\neq}_{303K}\ (\text{kJ mol}^{-1}) = 50.66\ r_V - 23.03\ (r = 0.997) \quad (1)$$

stronger donor capacity of the dimethylamino group. In this respect, further investigations[17] on butadienes **5** with cyclic *ortho*-amino substituents X = N(CH$_2$)$_n$ (n = 3–5) are worth mentioning. For these compounds, we also found unexpectedly high barriers to C-3–C-aryl rotations. The lower substituents show surprisingly the largest values resulting in the following range ($\Delta G^{\neq}_{303K}$ in kJ mol^{-1}, n = 3,4: 0.05 M in $CDBr_3$, n = 5: 0.05 M in CD_2Cl_2) (Scheme 4).



n	$\Delta G^{\#}_{303K}$
3	73
4	69
5	62

Scheme 4

There are no van der Waals data for an 1-naphthyl group as in **5i**. From the barrier to rotation an effective radius of 1.88 Å can be obtained which is in the range found for *n*-alkyl groups.[16]

By extrapolation to the radius of the H atom[15] the $\Delta G^{\neq}_{303K}$ value for the unsubstituted compound **5d** can be estimated to be 38 kJ mol^{-1}. In the same way, extrapolation for large substituents is possible. In the case of a *tert*-butyl group[16] the $\Delta G^{\neq}_{303K}$ can be estimated to be 100 kJ mol^{-1}. The evaluation of dependence of the C-3–C-aryl rotation on substituent sizes leads to the conclusion that a chirality axis stable at room temperature can only be realized by substituents larger than the *ortho*-*tert*-butyl group or if a second *ortho*-substituent is introduced. However, the preparation of *ortho*,*ortho'*-substituted phenylbutadienes in the same way as the mono-*ortho*-substituted compounds **5** was not possible.

Crystal structures of butadienes 3h, 4h and 6h‡

In addition to the C-3–C-aryl rotation in solution the crystal structures of the isopropyl-substituted compounds **3h**, **4h** and **6h** were studied (Tables 2 and 3). In the case of **3h** two molecules exist in the asymmetric unit, which show distinct differences especially in the bond lengths. Otherwise the distances are in the ranges corresponding to the push–pull character.[1]

With enhanced donor–acceptor interaction a bonding balance along the butadiene chain is already observed for single donor-amino substitution. With double amino substitution the formal C-2–C-3 and C-4–C-5 double bonds become longer than the formal C-2–C-3 single bond. The most important

‡ CCDC reference numbers 171037–171039. See http://www.rsc.org/suppdata/p2/b1/b107402b/ for crystallographic files in .cif or other format.

Table 2 Selected atom distances (Å) and torsion angles (deg) of the compounds **3h**, **4h** and **6h**

	Atom distances/Å				Torsion angles/deg			
	C-2–C-3	C-3–C-4	C-4–C-5	C-3–C-aryl	C-2–C-3[a]	C-3–C-4[b]	C-4–C-5[c]	C-3–C-aryl[d]
3h	1.366(4)	1.427(3)	1.364(4)	1.500(3)	5.8(4)	−175.1(3)	0.1(5) −177.6(2)	89.8(4)
	1.382(3)	1.427(4)	1.367(4)	1.478(4)	5.4(4)	−173.3(3)	−4.4(4) 177.1(2)	88.3(3)
4h	1.385(3)	1.409(3)	1.389(3)	1.496(3)	6.6(4)	−164.9(2)	31.1(3) −155.4(2)	−108.2(3)
6h	1.431(4)	1.354(4)	1.459(4)	1.503(4)	6.3(5)	5.7(5)	64.9(4) −117.4(3)	84.8(3)

[a] θ(CN(*Z*)–C-2–C-3–C-4). [b] θ(C-2–C-3–C-4–C-5). [c] θ(C-3–C-4–C-5–Do). [d] θ(C-2–C-3–C-aryl–C-*ortho*-aryl-X).

Table 3 Selected crystallographic data for the butadienes **3h**, **4h** and **6h**

	3h	**4h**	**6h**
Sum formula	$C_{17}H_{18}N_2S_2$	$C_{18}H_{21}N_3S$	$C_{23}H_{28}N_4$
M_w	314.46	311.44	360.49
Crystal size/mm	0.66 × 0.40 × 0.12	0.78 × 0.70 × 0.40	0.48 × 0.20 × 0.15
Colour	Yellow	Yellow	Yellowish
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, *b*, *c*/Å	9.466(2), 11.727(2), 17.473(3)	8.842(1), 11.368(1), 17.832(3)	8.154(1), 12.041(1), 12.445(1)
α, β, γ/deg	86.51(3), 76.31(3), 67.13(3)	90.00, 96.24(1), 90.00	104.28(1), 102.50(1), 106.54(1)
V/Å^3	1735.3(6)	1781.8(4)	1079.7(2)
Z	4	4	2
D_c/g cm^{-3}	1.204	1.161	1.109
Abs. coefficient μ/mm^{-1}	0.302	0.182	0.067
F(000)	664	664	388
T Data collection/K	298	298	298
2θ Range/deg	3.78–45.00	4.26–45.00	4.22–44.00
h, *k*, *l* Ranges	−5/10, −6/12, −18/18	0/9, 0/12, −19/19	0/8, −12/12, −13/12
Reflections total	3121	2342	2652
Reflections obsd. (>2σI)	2728	2013	1875
R(int)	0.0213	0.0305	0.032
Parameters refined	380	200	245
Final *R* (all, obsd.)	0.0411, 0.0360	0.0518, 0.0445	0.0829, 0.0552
Final R_w (all, obsd.)	0.0990, 0.0944	0.1257, 0.1189	0.1561, 0.1347
GOF on F^2	1.024	1.062	1.030

structural differences to the unsubstituted butadienes[3b] are the *Z*-arrangement of the methylthio group in **4h** and the s-*cis* conformation of **6h** (Fig. 5). The s-*cis* conformation favoured for **6h**

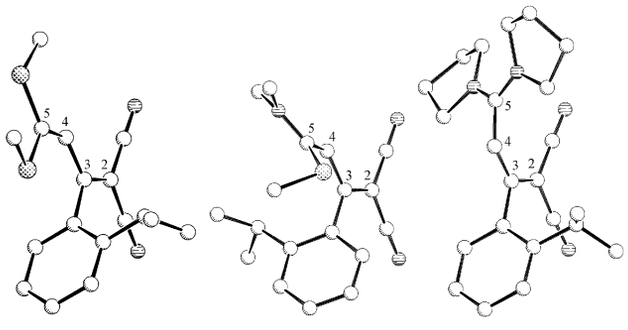


Fig. 5 Molecular structures of the butadienes **3h**, **4h** and **6h** (without H atoms).

was also found in solution (s-*cis* : s-*trans* = 95 : 5). Compared to **3h** a strong increase of the torsion angle about the C-4–C-5 bond of the aminobutadiene **4h** and **6h** was observed, and for **4h** additionally a C-3–C-aryl angle (Table 2).

Molecular modelling

For the mechanism of the C-3–C-aryl rotation semiempirical AM1-calculations[18] were made for compound **3h**. First the GS geometry for the gas phase was optimized based on the crystal structure data (Fig. 5). The torsion angle of C-2–C-3–C-1′–C-2′ was about 90°. Starting with 90° we have varied θ(C-2–C-3–C-1′–C-2′) in 15° steps, in the range of TS in 5° steps, and optimized the geometries (Fig. 6).

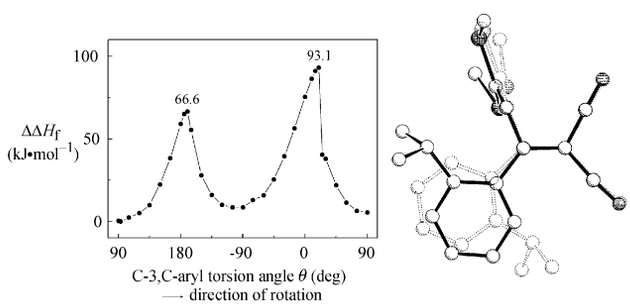


Fig. 6 Enthalpy difference $\Delta\Delta H_f = \Delta H_f - \Delta H_{f,min}$ (kJ mol^{-1}) of **3h** as a function of the torsion angle of C-2–C-3–C-1′–C-2′. AM1-optimized geometries (figure without H atoms) of both TS (plain figure, θ = −170°, $\Delta\Delta H_f$ = 66.6 kJ mol^{-1}; dotted figure, θ = 20°, $\Delta\Delta H_f$ = 93.1 kJ mol^{-1}).

As already discussed two TS were calculated with planar arrangements of the phenyl ring towards the butadiene plane. For **3h**, the energy for arrangement of X = *i*-Pr on the donor side is about 30 kJ mol^{-1} lower than for arranging on the acceptor side. The activation enthalpy $\Delta H^{\neq} = \Delta\Delta H_{f,max}$ of the energetically lower TS (67 kJ mol^{-1}) corresponds to the value obtained from dynamic NMR measurements ($\Delta H^{\neq}$ = 69 kJ mol^{-1}, Table 1). In Fig. 6 there are differences between the three

GS minima. The reason should be that in the TS there is a nearly orthogonal arrangement of the butadiene chain, which is not retained in the following optimization cycles. However the enthalpies are only 5–9 kJ mol^{-1} above the minimum (s-*trans* conformation) and characterize the very low C-3–C-4 rotation barrier.

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