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# $^{1}H$, $^{13}C$ and $^{15}N$ NMR Studies on the π-Electron Distribution and Intramolecular Mobility of Aminobuta-1,3-dienes†

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**The $^{1}H$, $^{13}C$ and $^{15}N$ NMR spectra of a series of 5-alkylthio-3-aryl-2-cyano-5-dialkylaminopenta-2,4-dienenitriles (4 and 5) with different amino and aryl substituents were recorded. The NMR chemical shifts are correlated with electronic effects of the substituents on the donor side of the butadiene system and also the *para*-phenyl substituents X. Dynamic $^{1}H$ and $^{13}C$ NMR measurements showed rotational processes about the C-2,C-3, C-3,C-4, C-4,C-5 and C-5,N bonds in 4 and 5, the kinetic and thermodynamic parameters of which were determined by lineshape analysis. The assignment of the lineshape alterations was made on the basis of signal intensities and separations and from the influence of the donor substituents, the phenyl substituents X and the solvents on the energy barriers.**


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*Keywords:* NMR; $^{1}H$ NMR; $^{13}C$ NMR; $^{15}N$ NMR; dynamic NMR; restricted C,C and C,N rotation; push–pull butadienes

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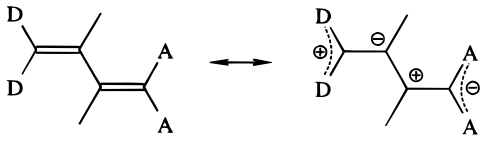
## INTRODUCTION

Butadienes of type **I** (so-called push–pull butadienes, A = acceptor groups; D = donor groups) represent a special class of compounds characterized by a marked π-electron interaction between the donor and acceptor groups and the butadiene double bonds described by structure **Ib** (Scheme 1).[1–14]

As a consequence of the electron interaction, three characteristics can be outlined: (i) the alternating charge distribution at the C-atoms (polymethine structure), reflected in the $^{13}C$ chemical shifts; (ii) a marked decrease in the barrier to rotation about the double bonds compared with normal butadienes; and (iii) an increase in the barrier to rotation about the single bonds. Hence these compounds are very interesting for dynamic NMR studies.

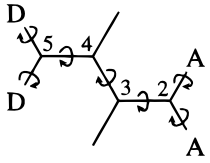
Theoretically, the following processes have to be taken into consideration: rotations about the C-2,C-3, C-3,C-4 and C-4,C-5 bonds and, considering the donor and acceptor groups also, rotations about the C-2,A and C-5,D bonds (Scheme 2).



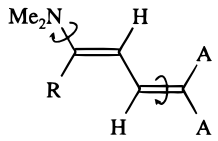
**Ia** **Ib**

**Scheme 1**

Many years ago, Prokof'ev *et al.*[3] investigated the butadiene derivatives **1** with the acceptor groups COR, COOR and $NO_2$ (Scheme 3). For these compounds, besides in addition to the restricted rotation of the dimethylamino group, also the rotation about the C-2,

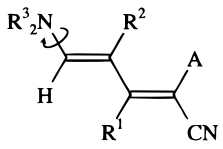


**Scheme 2**



A: COR, COOR, $NO_2$
R: H, Me, Ph

**1**



A: CN, COOR
$R^1$: H, alkyl, aryl
$R^2$: H, Me; $R^3$: alkyl

**2**

**Scheme 3**

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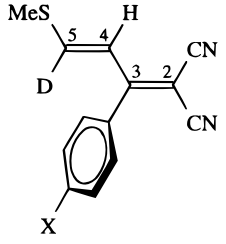
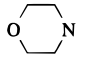
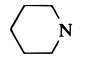
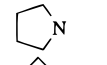
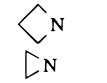
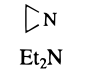



**3** D = MeS
**4,5** D = $R_2N$

| 3,4 | $R_2N$ | X |
|---|---|---|
| **a** | $Me_2N$ | $NO_2$ |
| **b** | $Me_2N$ | Br |
| **c** | $Me_2N$ | Cl |
| **d** | $Me_2N$ | H |
| **e** | $Me_2N$ | Me |
| **f** | $Me_2N$ | MeO |
| **g** | $Me_2N$ | $Me_2N$ |

| 5 | $R_2N$ | X |
|---|---|---|
| **a** |  | H |
| **b** |  | H |
| **c** |  | H |
| **d** |  | H |
| **e** |  | H |
| **f** | $Et_2N$ | H |

**Scheme 4**

C-3 bond was found to be observable because of the stronger electron delocalizing capacity of the acceptor groups.

For the amino compounds **2**, for the kinetic data only the rotation process about the C-5,N bond could be determined by dynamic $^1H$ and $^{13}C$ NMR (Scheme 3).[1]

In a previous study,[6] we found for the bis(methylthio)-substituted compounds **3** the rotation process on the C-4,C-5 bond to be within the NMR time-scale (Scheme 4). The values of the free energy of activation, $\Delta G^{\neq}$, for that process were found to be significantly dependent on the phenyl substituent X at the C-3 position. We also reported[6] the first dynamic NMR result for one example of the aminobutadienes **4** (**4f**, X = OMe). For **4f**, two dynamic processes were found with energies of activation of about 40 kJ $mol^{-1}$, which were assigned to the restricted rotation of the dimethylamino group and the rotation about the C-4,C-5 double bond. However, the results of a later investigation on another compound (**4a**, $X = NO_2$) made this assignment doubtful. Possibly the lineshape alterations observed for **4f** could be assigned to the restricted rotation about the central C-3,C-4 bond. Therefore, a systematic NMR study of **4** and **5** with different substituents X and R, considering the influence of substituents on the NMR and activation parameters, seemed to be necessary. This is the subject of the present paper.

## EXPERIMENTAL

### Spectra

The NMR measurements were performed with solutions of **4** and **5** on a Bruker ARX-300 spectrometer ($^1H$, 300.1 MHz, sweep width 3 kHz; $^{13}C$, 75.5 MHz, sweep width 15 kHz; $^{15}N$, 30.4 MHz, sweep width 10 kHz, delay time 30 s). The recording of $^{15}N$ NMR spectra was performed with natural-abundance compounds **4** using the inverse-gated decoupling technique. Solvents given in Tables 1–6 were dried with molecular sieves or sodium sulphate and the halogen-containing solvents were purified with basic aluminium oxide to remove acid impurities; concentrations were 0.05 M for $^1H$ and $^{13}C$ and 0.5 M for $^{15}N$; the temperature was 303 K.

For low-temperature measurements argon was bubbled through the solution to remove paramagnetic oxygen. The probe temperature was measured by means of thermometer liquids.[15] The exchange rates at the coalescence point were obtained for equally populated sites using the Gutowsky–Holm relationship[16] and, for unequal populations, using the equations of Shanan-Atidi and Bar-Eli.[17] The free energies of activation were calculated from the Eyring equation. The errors in $\Delta G_c^{\neq}$ were estimated to be $\pm 0.8$ kJ $mol^{-1}$.

### Compounds

The preparation of compounds **4a–f**, **5a–c** and **f** was described previously.[18] Compounds **4g** and **5d** and **e** were prepared according to the procedure described previously[18] in a modified version.

**Preparation of 4g.** *2-[1-(4-Dimethylaminophenyl)ethylidene]malononitrile.* A solution of 1.63 g (10 mmol) of 4-dimethylaminoacetophenone[19] and 1.32 g (20 mmol) of malononitrile in 20 ml of toluene was refluxed for 72 h in the presence of 0.24 g (4 mmol) of acetic acid and 0.08 g (1 mmol) of ammonium acetate, replacing the catalysts mixture every 8–10 h. The reaction product was washed with water and dried over sodium sulphate. Purification by column chromatography ($SiO_2/CHCl_3$) and recrystallization from ethanol yielded 1.14 g (54%) of orange needles, m.p. 118–120 °C. $^1H$ NMR: 2.56 (s, 3H, Me), 3.07 (s, 6H, $NMe_2$), 6.68 (m, 2H, Ph-*m*), 7.67 (m, 2H, Ph-*o*). $^{13}C$ NMR: 22.9 (Me), 39.9 ($NMe_2$), 76.8 (C-2), 111.1 (Ph-*m*), 114.7 (CN), 115.1 (CN), 122.1 (Ph-*i*), 130.3 (Ph-*o*), 153.2 (Ph-*p*), 172.1 (C-3).

*2-Cyano-3-(4-dimethylaminophenyl)-5,5-bis(methylthio)penta-2,4-dienenitrile* (***3g***). Compound **3g** was prepared by a modified earlier procedure.[20] In an inert gas atmosphere, 0.53 g (2.5 mmol) 2-[1-(4-dimethylaminophenyl)ethylidene]malononitrile, 0.38 g (5 mmol) carbon disulphide and 1.78 g (12.5 mmol) methyl iodide in 15 ml of absolute dimethylformamide were added, with stirring, to 0.15 g (6.25 mmol) of sodium hydride. After stirring for 1 h the reaction mixture was placed in 50 ml of ice–water and left to stand for several days to crystallize. The precipitate was separated, washed with water and light petroleum and recrystallized from ethanol. Yield: 0.56 g (71%), dark-red crystals, m.p. 150–151 °C. $^1H$ NMR: 2.30 (s, 3H, SMe), 2.55 (s, 3H, SMe), 3.06 (s, 6H, $NMe_2$), 6.41 (s, 1H, H-4), 6.68 (m, 2H, Ph-*m*), 7.40 (m, 2H, Ph-*o*). $^{13}C$ NMR: 16.9 (SMe), 17.6 (SMe), 40.0 ($NMe_2$), 73.7 (C-2), 111.4 (Ph-*m*), 115.4 (CN), 115.9 (CN), 116.5 (C-4), 121.2 (Ph-*i*), 131.6 (Ph-*o*), 153.1 (Ph-*p*), 159.5 (C-5), 167.9 (C-3).

*2-Cyano-3-(4-dimethylaminophenyl)-5-dimethylamino-5-methylthiopenta-2,4-dienenitrile* (***4g***). A 4 ml volume of a solution of dimethylamine in water (40%) was added to 0.32 g (1 mmol) of **3g** in 4 ml of THF during 3 h with stirring and refluxing. The crystals that precipitated on cooling were recrystallized from ethanol. Yield: 0.22 g (70%), yellow crystals, m.p. 184–186 °C. $^1H$ and $^{13}C$ NMR: see Table 1.

**Preparation of 5d and 5e.** *5-(Azetidinyl)-2-cyano-5-methylthio-3-phenylpenta-2,4-dienenitrile* (***5d***). A 0.55 g (2 mmol) amount of **3d** and 0.23 g (4 mmol) of azetidine in 8 ml of THF were refluxed with stirring for 20 min. The solvent was removed and the solid residue obtained after addition of ethanol was recrystallized from ethanol. Yield: 0.43 g (76%), violet crystals, m.p. 104–107 °C. $^1H$ and $^{13}C$ NMR: see Table 2.

*5-(Aziridinyl)-2-cyano-5-methylthio-3-phenylpenta-2,4-dienenitrile* (***5e***). A 1.34 g (5 mmol) amount of **3d** and 0.43 g (10 mmol) of aziridine in 8 ml of THF were stirred at room temperature for 4 h. The mixture was then purified by column chromatography ($SiO_2/CH_2Cl_2$).

Further, 0.44 g (33%) of **5e**, 0.58 g (43%) of **3d** and 0.09 g (7%) of the di(aziridinyl)butadiene were separated. A well timed discontinuation of the reaction and immediate purification are necessary to prevent complete conversion into the di-product and a cyclisation product. Recrystallization from ethanol yielded violet crystals, m.p. 100–118 °C (decomposition). $^1$H and $^{13}$C NMR: see Table 2.

## RESULTS AND DISCUSSION

### Influence of different donor and phenyl substituents on the ground state of compounds 4 and 5

The $^1$H, $^{13}$C and $^{15}$N chemical shifts of compounds **4** and **5** (Tables 1–4) imply a considerable $\pi$-electron interaction corresponding to structure **Ib**. Several NMR signals support this fact, e.g. the signal of H-4, the $^{13}$C signals of the butadiene carbon atoms and the $^{15}$N signal of the amino group.[7] Additionally, the strongly alternating $^{13}$C chemical shifts of the butadiene carbon atoms prove the polymethine structure of the compounds investigated, which is induced by the push–pull property of the substituents at C-2 and C-5, i.e. the cyano, amino and methylthio groups. Therefore, these substituents cause the transition from the polyene state of unsubstituted butadiene with balanced $\pi$-electron densities to the polymethine state with alternating $\pi$-electron densities.[21,22]

The $\pi$-electron interaction is increased by substituents with higher donor capacity at C-5. Therefore, the replacement of a methylthio group of **3** by an amino group, resulting in **4**, leads to characteristic high-field shifts for H-4, C-2 and C-4, whereas downfield shifts are found for the C-5 and CN signals (Table 1). The same alteration in chemical shifts can be observed by increasing the donor strengths of the *N*-substituents in **5a–f** (Table 2), including **4d** (Table 1).

The dependence of the NMR chemical shifts on the nature of phenyl substituents X in **4** shows that the phenyl ring is included in the conjugation of the butadiene system. Correlations of H-4 and C-1 to C-4 with Hammett's $\sigma_p$ constants has been demonstrated previously.[6,7]

Because of the higher sensitivity of the $^{15}$N nuclei to changes in chemical environment, the $^{15}$N chemical shifts of the amino group on the donor side, and of cyano groups on the acceptor side (Table 3), are particularly important for conclusions about the structure of the butadienes **4** and **5**. In such conjugated systems, in particular, the extent of n–$\pi$ interaction of the lone pair of nitrogen with the $\pi$-electrons of the C,C double bond contributes to this sensitivity. The $\delta^{15}$N values of about $-270$ ppm for the donor nitrogen are in the range of amides and enamino ketones,[23] pointing to a strong n–$\pi$ interaction. With increase in the donor strength of the *para*-phenyl substituent of **4** the $^{15}$N signal is shifted to higher field. The same is true for the $^{15}$N signals of the cyano groups. As for $^{13}$C chemical shifts, a Hammett correlation was also found for the $^{15}$N chemical shifts.

Compared with Ref. 7, the $\delta^{15}$N values of the $NMe_2$ group were shifted to higher field by 0.4–1.4 ppm. This prompted a study of the dependence of $^{15}$N chemical

**Table 1. $^1$H and $^{13}$C chemical shifts δ (ppm, TMS = 0 ppm) of compounds 4 (3d for comparison) in $CDCl_3$**

| | 3d | 4a | 4b | 4c | 4d | 4e | 4f | 4g |
|---|---|---|---|---|---|---|---|---|
| H-4 | 6.52 | 5.42 | 5.32 | 5.32 | 5.35 | 5.31 | 5.28 | 5.21 |
| $SCH_3$ | 2.59; 2.28 | 2.21 | 2.27 | 2.27 | 2.29 | 2.31 | 2.32 | 2.34 |
| $NCH_3$ | — | 3.22 | 3.12 | 3.12 | 3.06 | 3.05 | 3.05 | 3.02 |
| Other signals | [a] | [b] | [c] | [d] | [e] | [f] | [g] | [h] |
| C-2 | 77.4 | 63.3 | 62.5 | 62.6 | 62.7 | 61.6 | 61.8 | 60.4 |
| C-3 | 167.7 | 165.8 | 167.3 | 167.3 | 168.8 | 168.8 | 168.5 | 169.2 |
| C-4 | 113.8 | 98.9 | 97.9 | 97.9 | 97.9 | 97.5 | 97.3 | 96.7 |
| C-5 | 165.5 | 171.9 | 172.6 | 172.6 | 172.6 | 172.7 | 172.6 | 171.8 |
| CN | 114.4 | 116.7 | 117.4 | 117.4 | 117.6 | 117.9 | 118.1 | 118.7 |
| CN | 114.0 | 116.4 | 117.1 | 117.1 | 117.4 | 117.6 | 117.7 | 118.3 |
| $SCH_3$ | 17.7; 16.6 | 18.5 | 18.4 | 18.4 | 18.4 | 18.3 | 18.4 | 18.3 |
| $NCH_3$ | — | 43.2 | 43.2 | 43.2 | 43.2 | 43.1 | 43.1 | 43.0 |
| Other signals | [i] | [j] | [k] | [l] | [m] | [n] | [o] | [p] |

[a] 7.42–7.54 (m, 3H, Ph-*o*, Ph-*p*), 7.32–7.36 (m, 2H, Ph-*m*).
[b] 7.58 (m, 2H, Ph-*o*), 8.26 (m, 2H, Ph-*m*).
[c] 7.29 (m, 2H, Ph-*o*), 7.53 (m, 2H, Ph-*m*).
[d] 7.33–7.40 (m, 4H, Ph-*o*, Ph-*m*).
[e] 7.38–7.45 (m, 5H, Ph).
[f] 2.38 (s, 3H, Me), 7.31 (m, 2H, Ph-*o*), 7.19 (m, 2H, Ph-*m*).
[g] 3.84 (s, 3H, OMe), 7.39 (m, 2H, Ph-*o*), 6.91 (m, 2H, Ph-*m*).
[h] 3.02 (s, 6H, $NMe_2$), 7.36 (m, 2H, Ph-*o*), 6.65 (m, 2H, Ph-*m*).
[i] 134.5 (Ph-*i*), 128.5 (Ph-*o*), 129.0 (Ph-*m*), 131.1 (Ph-*p*).
[j] 144.0 (Ph-*i*), 130.1 (Ph-*o*), 123.5 (Ph-*m*), 148.8 (Ph-*p*).
[k] 136.2 (Ph-*i*), 130.7 (Ph-*o*), 131.6 (Ph-*m*), 125.2 (Ph-*p*).
[l] 135.7 (Ph-*i*), 130.5 (Ph-*o*), 128.7 (Ph-*m*), 136.8 (Ph-*p*).
[m] 137.2 (Ph-*i*), 129.2 (Ph-*o*), 128.4 (Ph-*m*), 130.7 (Ph-*p*).
[n] 21.3 (Me), 134.1 (Ph-*i*), 129.1 (Ph-*o*), 129.0 (Ph-*m*), 141.1 (Ph-*p*).
[o] 55.4 (OMe), 129.2 (Ph-*i*), 131.0 (Ph-*o*), 113.8 (Ph-*m*), 161.9 (Ph-*p*).
[p] 40.0 ($NMe_2$), 123.7 (Ph-*i*), 131.1 (Ph-*o*), 111.1 (Ph-*m*), 152.4 (Ph-*p*).

**Table 2. $^{1}H$ and $^{13}C$ chemical shifts δ (ppm, TMS = 0 ppm) of compounds 5 in $CDCl_3$**

| | 5a | 5b | 5c | 5d | 5e[a] | 5f |
|---|---|---|---|---|---|---|
| H-4 | 5.59 | 5.52 | 5.13 | 5.20 | 5.87; 6.33 | 5.59 |
| $SCH_3$ | 2.29 | 2.30 | 2.29 | 2.27 | 2.52; 2.27 | 2.17 |
| $NCH_2$ | 3.31 m (4H) | 3.29 m (4H) | 3.47 m (4H) | 4.01 t (4H) | 1.69 s (4H); 2.39 s (4H) | 3.53 q (4H) |
| Other signals | [b] | [c] | [d] | [e] | [f] | [g] |
| C-2 | 66.7 | 64.0 | 57.8 | 62.1 | 73.9; 75.4 | 63.3 |
| C-3 | 169.2 | 169.0 | 166.3 | 167.6 | 167.4; 170.1 | 169.2 |
| C-4 | 99.1 | 98.3 | 96.8 | 94.5 | 102.4; 107.8 | 97.5 |
| C-5 | 170.8 | 171.9 | 169.5 | 167.4 | 173.3; 172.2 | 171.8 |
| CN | 116.6 | 117.5 | 118.4 | 117.8 | 115.3; 114.8 | 117.6 |
| CN | 116.5 | 117.5 | 117.7 | 117.2 | 114.9; 114.4 | 117.6 |
| $SCH_3$ | 17.6 | 17.9 | 18.3 | 17.5 | 16.3; 15.1 | 19.4 |
| $NCH_2$ | 52.0 | 53.4 | 52.6 | 54.8 | 31.7; 31.3 | 47.7 |
| Other signals | [h] | [i] | [j] | [k] | [l] | [m] |

[a] The first value refers to the more intense signal.
[b] 3.51 (m, 4H, $CH_2O$), 7.35–7.49 (m, 5H, Ph).
[c] 1.53 (m, 6H, $CH_2$), 7.33–7.46 (m, 5H, Ph).
[d] 2.01 (m, 4H, $CH_2$), 7.32–7.46 (m, 5H, Ph).
[e] 2.35 (m, 2H, $CH_2$), 7.37–7.46 (m, 5H, Ph).
[f] 7.42–7.50 (m, 5H, Ph); 7.42–7.50 (m, 3H, Ph), 7.27 (m, 2H, Ph-*o*).
[g] 1.19 (t, 6H, $CH_3$), 7.33–7.47 (m, 5H, Ph).
[h] 65.9 ($CH_2O$), 135.9 (Ph-*i*), 128.9 (Ph-*o*), 128.3 (Ph-*m*), 130.8 (Ph-*p*).
[i] 26.0; 24.0 ($CH_2$), 136.7 (Ph-*i*), 129.2 (Ph-*o*), 128.4 (Ph-*m*), 130.6 (Ph-*p*).
[j] 25.2 ($CH_2$), 137.5 (Ph-*i*), 129.3 (Ph-*o*), 128.1 (Ph-*m*), 130.4 (Ph-*p*).
[k] 15.9 ($CH_2$), 136.9 (Ph-*i*), 129.4 (Ph-*o*), 128.4 (Ph-*m*), 130.8 (Ph-*p*).
[l] 135.0; 134.9 (Ph-*i*), 128.6; 128.5 (Ph-*o*), 129.0; 129.0 (Ph-*m*), 130.9; 130.8 (Ph-*p*).
[m] 13.2 ($CH_3$), 136.6 (Ph-*i*), 129.3 (Ph-*o*), 128.2 (Ph-*m*), 130.6 (Ph-*p*).

**Table 3. $^{15}N$ chemical shifts δ (ppm, $MeNO_2$ = 0 ppm) of compounds 4 and 5 in $CDCl_3$**

| | 3d | 4a | 4b | 4c | 4d | 4e | 4f | 4g |
|---|---|---|---|---|---|---|---|---|
| CN | −115.6 | −120.6 | −122.1 | −122.1 | −122.9 | −123.4 | −123.7 | −124.8 |
| CN | −111.6 | −115.2 | −116.6 | −116.7 | −117.4 | −117.8 | −118.1 | −119.7 |
| $NCH_3$ | | −266.8 | −269.7 | −269.9 | −271.2 | −272.2 | −272.9 | −277.2 |
| Other signals | | [a] | | | | | | [b] |

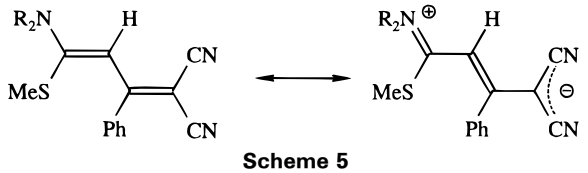
| | 5a | 5b | 5c | 5d | 5e[c] | 5f |
|---|---|---|---|---|---|---|
| CN | −120.6 | −122.4 | −124.5 | −123.4 | −118.1; −118.4 | −123.0 |
| CN | −115.6 | −117.2 | −118.0 | −117.2 | −113.4; −113.2 | −117.8 |
| $NCH_2$ | −270.2 | −253.9 | −235.3 | −245.3 | | −242.3 |

[a] −40.1 ($NO_2$).
[b] −327.2 ($PhNCH_3$).
[c] The first value refers to the more intense signal. The $NCH_2$ signals could not be observed since **5e** completely cyclized in a short time.

shifts on concentration in the case of **4d**. In the range 0.25–1.5 mol $l^{-1}$, we found an approximately linear low-field shift of the $NMe_2$ signal of about 4 ppm, whereas the CN signals remained constant (Table 4). In the compounds **5** the $^{15}N$ signals of the amino groups shifted to lower field with increasing n–π interactions. In contrast, the $^{15}N$ signals of the cyano groups shifted to higher field (Scheme 5). The donor character of the amino groups can be derived from the data obtained. The largest donor effect can be assigned, therefore, to the pyrrolidino group in **5c**. The strong high-field shift of the $NMe_2$ signal in **4d** is remarkable and is caused by a reduced n–π overlap of the dimethylamino group with the butadiene chain.

**Table 4. $^{15}N$ chemical shifts δ (ppm, $MeNO_2$ = 0 ppm) of 4d in $CDCl_3$**

| Concentration (mol $l^{-1}$) | $NMe_2$ | CN | CN |
|---|---|---|---|
| 0.25 | −272.6 | −123.0 | −117.4 |
| 0.5 | −271.2 | −122.9 | −117.4 |
| 0.75 | −270.6 | −123.0 | −117.4 |
| 1.0 | −269.8 | −122.9 | −117.3 |
| 1.25 | −269.2 | −122.9 | −117.3 |
| 1.5 | −268.7 | −123.0 | −117.4 |




**Scheme 5**

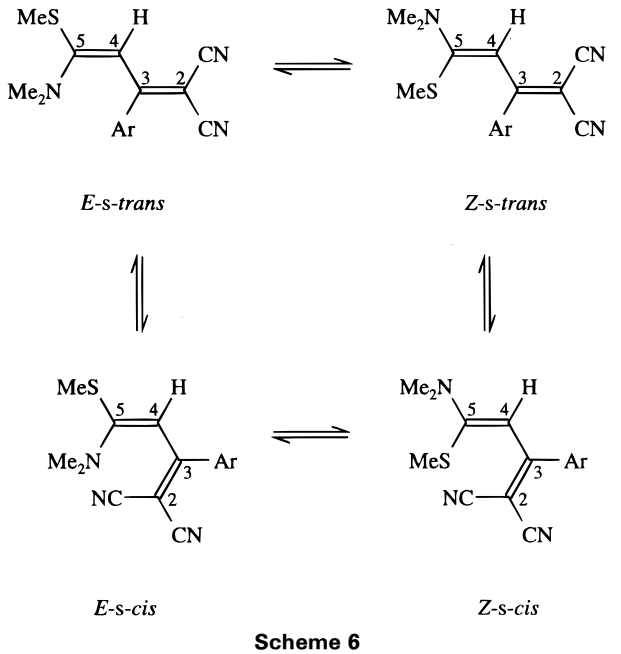
 

The aziridinyl compound **5e** shows a doubling of signals with an intensity ratio of about 2:1 in the $^{1}H$, $^{13}C$ and $^{15}N$ NMR spectra because of hindered rotation about the C-4,C-5 bond (see below). The more intense signal can be assigned to the *E* configuration, taking into consideration the anisotropic effect of the phenyl group (Scheme 6). The reason of this can be seen by comparison of the NMR data for H-2,C-2 and C-4 of both isomers. Therefore, stronger donor–acceptor interactions exist in the *E* isomer. Nevertheless, the aziridinyl group has by far the weakest donor effect of the butadienes **5**.

## Dynamic NMR results for the aminobutadienes 4 and 5

In the temperature range from −100 to 100 °C, characteristic lineshape alterations of various signals in the $^{1}H$ and $^{13}C$ spectra of **4** and **5** were observed. They could be assigned to the rotation processes about the C-2,C-3, C-3,C-4, C-4,C-5 and C-5,N bonds. The results of the dynamic NMR measurements are given in Tables 5 and 6.

**Compounds 4.** The rotational processes about the C-3,C-4, C-4,C-5 and C-5,N bonds were detectable from the dynamic $^{1}H$ NMR spectra. The lineshape alterations of the SMe, $NMe_2$ and H-4 signals gave the barriers to rotation. The splitting patterns of signals of all compounds **4** are similar and, therefore, will be discussed only for the example of **4d** (Fig. 1). In the $^{1}H$ NMR spectrum at room temperature, averaged signals from all exchange processes are observed. On cooling, between 211 and 201 K the decoalescence points of the C-3,C-4 rotation can be observed from the signals of SMe, $NMe_2$ and H-4, and also the C-5,N rotation from the $NMe_2$ signals. At 211 K, the H-4 signal is split into two in the ratio 0.68:0.32 (high field) with a separation of $\Delta\nu_c = 229$ Hz. For the $NMe_2$ group, a splitting was found at 210 and 201 K, forming four signals. These signal pairs have a population ratio of 0.68 (high field):0.32, which is the reverse of that of the H-4 signal splitting. The coalescence point of the SMe signals is observed at 201 K with the population ratio also the reverse of that of H-4. The more intense signals had to be assigned to the *s-trans*-butadiene (Scheme 6). These signals show a further splitting at *ca.* 160 K due to the restricted C-4,C-5 rotation. They were partly overlapped after splitting, but it could be ascertained that the signals with the larger population in the case of $NMe_2$ and H-4 were shifted to higher field and in the case of SMe to lower field. The more intense signals must be assigned to the *E* configuration about the C-4, C-5 bond. The *s-cis*-butadiene does not show any further exchange process down to 160 K.




**Scheme 6**

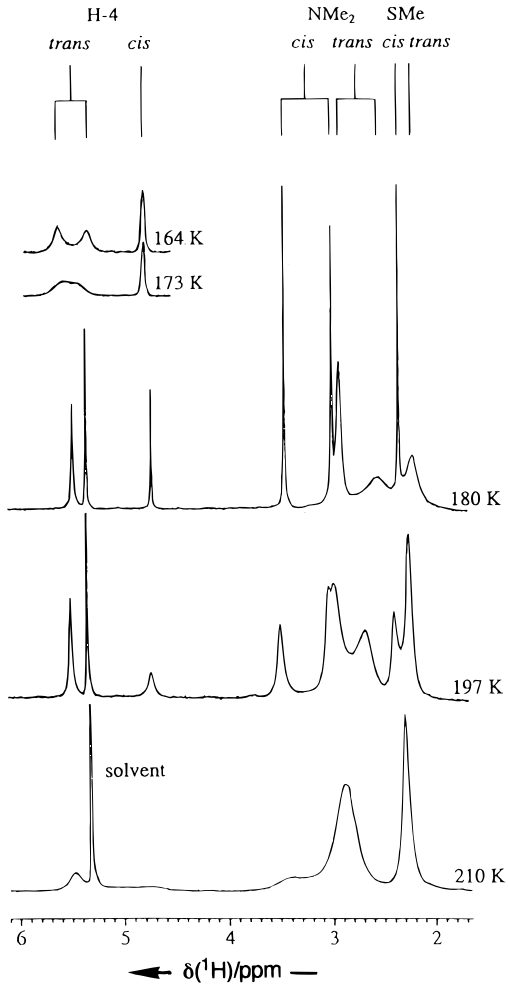



**Figure 1.** Temperature-dependent $^{1}H$ NMR spectra of **4d** in $CD_2Cl_2$ (180–210 K) and THF-$d_8$ (164–173 K).

The assignment of the lineshape alterations was made unambiguously on the basis of signal intensities and separations and also from the influence of the donor substituents, the phenyl substituents X and of the solvents on the energy barriers.

The hindered C-5,N rotation is characterized by a splitting of the $NMe_2$ signals into equally intense signals. The C-3,C-4 and C-4,C-5 rotation processes can be distinguished by means of the anisotropy effects of the twisted phenyl ring[9,25] on the signals of neighbouring protons (Scheme 6). In the case of the C-3,C-4 rotation in the *s-trans*-butadiene, the donor groups are positioned in the shielding anisotropy cone of the

**Table 5. Dynamic NMR parameters and free energies of activation for the restricted rotations in the butadienes 4 (3d for comparison)**

| Compound | Solvent | Observed signal | $T_c$ (K) | $\Delta\nu_c$ (Hz) | $p_c$ [a] | $\Delta G_c^{\neq}$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | | Rotation about the C-2,C-3 bond | | | | |
| **4d** | DMF-$d_7$ | CN | 297 | 22 | — | 63.0 |
| | | Rotation about the C-3,C-4 bond | | | | |
| **4a** | $CD_2Cl_2$ | H-4 | 222 | 280 | 0.73 | 43.8; 42.0 |
| **4b** | $CD_2Cl_2$ | H-4 | 216 | 242 | 0.70 | 42.7; 41.2 |
| **4c** | $CD_2Cl_2$ | H-4 | 214 | 243 | 0.70 | 42.4; 40.9 |
| **4d** | $CD_2Cl_2$ | H-4 | 211 | 229 | 0.68 | 41.7; 40.4 |
| | THF-$d_8$ | H-4 | 199 | 208 | 0.69 | 39.4; 38.1 |
| **4e** | $CD_2Cl_2$ | H-4 | 207 | 220 | 0.68 | 40.9; 39.6 |
| **4f** | $CD_2Cl_2$ | H-4 | 203 | 213 | 0.67 | 40.1; 38.9 |
| **4g** | $CD_2Cl_2$ | H-4 | 184 | 165 | 0.67 | 36.6; 35.5 |
| | | Rotation about the C-4,C-5 bond, *s-trans* compound[b] | | | | |
| **3d** | $CDBr_3$ | SMe | | | | 96.8[24] |
| **4d** | $CD_2Cl_2$ | SMe | 161 | | | 31.6; 30.5 |
| | THF-$d_8$ | H-4 | 172 | 82 | 0.52[c] | 34.0; 33.9 |
| **4e** | $CD_2Cl_2$ | SMe | 165 | | | 32.6; 31.4 |
| **4f** | $CD_2Cl_2$ | SMe | 173 | | | 34.1; 32.9 |
| **4g** | $CD_2Cl_2$ | SMe | 175 | 190 | 0.68 | 34.6; 33.5 |
| | | Rotation about the C-5,N bond, *s-cis* compound | | | | |
| **4a** | $CD_2Cl_2$ | $NMe_2$ | 217 | 124 | — | 42.4 |
| **4b** | $CD_2Cl_2$ | $NMe_2$ | 213 | 133 | — | 41.4 |
| **4c** | $CD_2Cl_2$ | $NMe_2$ | 212 | 134 | — | 41.3 |
| **4d** | $CD_2Cl_2$ | $NMe_2$ | 210 | 133 | — | 40.9 |
| | THF-$d_8$ | $NMe_2$ | 197 | 134 | — | 38.1 |
| **4d**[d] | $CD_2Cl_2$ | $NMe_2$ | 201 | 190 | — | 38.4 |
| **4e** | $CD_2Cl_2$ | $NMe_2$ | 205 | 136 | — | 39.9 |
| **4f** | $CD_2Cl_2$ | $NMe_2$ | 201 | 138 | — | 39.0 |

[a] $p_c$ of *s-trans* (C-3,C-4) or *E* (C-4,C-5) compound, respectively.
[b] $\Delta G_c^{\neq}$ values of **4d–f** in $CD_2Cl_2$ were calculated with estimated $\Delta\nu_c = 200$ Hz and $p_{c,E} = 0.7$.
[c] $p_{c,E}$ and $p_{c,Z}$ exchangeable.
[d] *s-trans* compound.

phenyl ring, whereas in the *s-cis*-butadiene it is the proton H-4. Therefore, on splitting of the averaged signals below the coalescence temperature, a large $\Delta\nu_c$ of the corresponding signals results.

If the high-field and downfield signals of SMe and the $NMe_2$ groups have the same population ratio, which is opposite to that of the CH group, then the process observed can be assigned to the C-3,C-4 rotation. Analogously, for the C-4,C-5 rotation the population ratio of one donor group has to be opposite to that of the other donor group. Moreover, for H-4 in the case of C-4,C-5 rotation, the anisotropic effect of the phenyl ring remains the same and, therefore, low splittings $\Delta\nu_c$ are found.

The size of the energy barriers depends on both the ground state and transition state. It has been shown by crystal structure analysis of **4d** that the butadiene chain is in a nearly planar arrangement.[25] For this reason, optimum overlapping of the bonding p-orbitals of the C atoms is possible in the ground state. For the transition states, orthogonal arrangements can be formulated, raising the energy of the molecule owing to the loss of $\pi$-overlap. For push–pull systems such as **4** and **5**, bipolar transition states for the rotations about the C-2,C-3 and the C-4,C-5 bonds can be assumed, which are stabilized by donor and acceptor substituents because of delocalization of the positive and negative charges. Analogously, a polar mechanism should also be considered for the rotations about the C-3,C-4 and the C,N bonds, but here the ground state is more polar than the transition state. Therefore, the stabilizing effect of donor and acceptor substituents is preferred in the ground state. In the same way, the solvent effects on the sizes of energy barriers found in such systems can be interpreted as being caused by different extents of stabilization of the ground and transition states.

Thus, with increasing donor capacity of the substituents at the donor site, the extent of double-bond character and, therefore, the barrier to rotation about both the C-2,C-3 and the C-4,C-5 bonds in **4** and **5** should be lowered, whereas the barriers to C-3,C-4 and C-5,N rotation are expected to be raised. In the same way, with increasing electron withdrawal by the phenyl substituent X, the energy barriers should be influenced in the same direction. Likewise, more polar solvents should result in a decrease in the rotation barriers for both the C-2,C-3 and the C-4,C-5 bonds, but in an increase of those for the C-3,C-4 and C-5,N bonds.

For **4**, in comparison with **3**, an increase in the C-3,C-4 rotation barrier was found on replacing an SMe by an

**Table 6. Dynamic NMR parameters and free energies of activation for the restricted rotations in the butadienes 5**

| Compound | Solvent | Observed signal | $T_c$ (K) | $\Delta\nu_c$ (Hz) | $p_c$ [a] | $\Delta G_c^{\neq}$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | | Rotation about the C-2,C-3 bond | | | | |
| **5a** | DMF-$d_7$ | CN | 309 | 11 | — | 67.6 |
| **5c** | DMF-$d_7$ | CN | 301 | 41 | — | 62.5 |
| | | Rotation about the C-3,C-4 bond | | | | |
| **5a** | $CD_2Cl_2$ | H-4 | 180 ± 5 | 240 | 0.95 | 38.3; 33.9[b] |
| **5b** | $CD_2Cl_2$ | H-4 | 202 | 250 | 0.87 | 41.5; 38.3 |
| **5c** | $CD_2Cl_2$ | H-4 | 226 | 215 | 0.33 | 43.3; 44.7 |
| **5d** | $CD_2Cl_2$ | H-4 | 220 | 195 | 0.47 | 42.4; 42.6 |
| **5f** | $CD_2Cl_2$ | H-4 | 204 | 233 | 0.87 | 42.1; 38.9 |
| | | Rotation about the C-4,C-5 bond, *s-trans* compound | | | | |
| **5a**[c] | THF-$d_8$ | H-4 | 191 | 38 | 0.56 | 39.5; 39.1 |
| **5c** | THF-$d_8$ | H-4 | 166 | 72 | 0.59[d] | 33.5; 33.0 |
| **5e**[e] | $CDBr_3$ | H-4 | 371 | 126 | 0.63 | 77.0; 75.4 |
| | | Rotation about the C-5,N bond[f] | | | | |
| **5a** | $CD_2Cl_2$ | $NCH_2$ | 186 | 320 | — | 34.7 |
| **5b** | $CD_2Cl_2$ | $NCH_2$ | 191 | 175 | — | 36.5 |
| | $CD_2Cl_2$ | $NCH_2$ | 190 | 250 | — | 35.9 |
| **5c** | $CD_2Cl_2$ | $NCH_2$ | 227 | 108 | — | 44.7 |
| | $CD_2Cl_2$ | $NCH_2$ | 229 | 142 | — | 44.5 |
| **5d** | $CD_2Cl_2$ | $NCH_2$ | 213 ± 5 | 223 | — | 40.5[b] |
| **5f** | $CD_2Cl_2$ | $CH_3$ | 199 | 55 | — | 40.1 |
| | | Unknown exchange process[f] | | | | |
| **5a** | $CD_2Cl_2$ | $NCH_2$ | 232 | 450 ± 50 | — | 43.0 |
| **5b** | $CD_2Cl_2$ | $NCH_2$ | 249 | 450 ± 50 | — | 46.2 |
| **5c** | $CD_2Cl_2$ | $NCH_2$ | 252 | 155 | — | 49.0 |
| **5d** | $CD_2Cl_2$ | $NCH_2$ | 251 | 350 ± 50 | — | 47.3 |

[a] $p_c$ of *s-trans* (C-3,C-4) or *E* (C-4,C-5) compound, respectively.
[b] ±1.5 kJ mol$^{-1}$.
[c] C-3,C-4 exchange averaged.
[d] $p_{c,E}$ and $p_{c,Z}$ exchangeable.
[e] All data refer to 371 K (nearly 10 K below $T_c$, see text).
[f] **5a**, **f**, *s-trans*; **5c**, *s-cis*; **5b**, **d**, probably *s-trans*, but not finally cleared.

$NMe_2$ donor group (Table 5). Whereas **3d** did not show any evidence for this exchange process in the available low-temperature range, the two barriers of **4d** (*s-trans* → *s-cis* and *s-cis* → *s-trans*, Scheme 6) could be determined, being about 40 kJ mol$^{-1}$. A significant influence of the *para*-phenyl substituents X on the energy barrier of this process was established. Calculations yielded correlations of $\Delta G_c^{\neq}$ with the Hammett constants and $^{13}C$ and $^{15}N$ NMR chemical shifts (for the latter, see Fig. 2). The non-linearity follows from a finite $\Delta S^{\neq}$ but, without complete lineshape analyses (CLSA), no statement can be made about the size of the activation entropy. Nevertheless, lowering of the energy barrier of the C-3,C-4 rotation by an increasing donor capacity of X is unquestioned.

The barriers to C-5,N rotation (Table 5) were completely determined only for the *s-cis* compounds **4a**–**f** since the $NMe_2$ signals of the *s-trans* conformers already showed broadening because of the restricted C-4,C-5 rotation. The Hammett relationships regarding the C-3,C-4 rotation can be directly transferred to the C-5,N rotation because of the linear correlation between $\Delta G_c^{\neq}$ of both processes (correlation coefficient >0.99, Fig. 3). This indicates an equal transfer of the substituent effects along the butadiene chain.

For **4d**, in comparison with **3d**, a drastic lowering of the C-4,C-5 rotation barrier from 96 to 31 kJ mol$^{-1}$ was found (Table 5). The C-4,C-5 process could be determined in the investigated temperature interval only for **4d**–**g**. Coalescence points were observed only for the *s-trans* signals. The *s-cis* signals did not show any broadening, but this may also be attributed to a very small $\Delta\nu_c$, because the influence of the phenyl anisotropy regarding the donor groups is unchanged on C-4, C-5 rotation of the *s-cis*-butadienes. The higher barriers

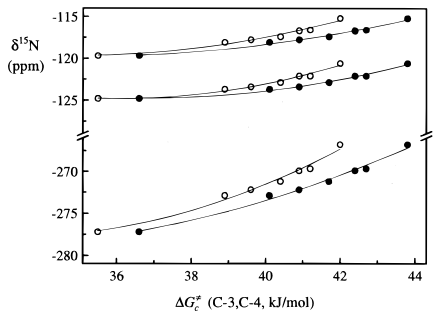



**Figure 2.** Correlations of $^{15}N$ chemical shifts and free energies of activation of the C-3,C-4 rotation in compounds **4** (●, *s-trans* → *s-cis*; ○, *s-cis* → *s-trans*).

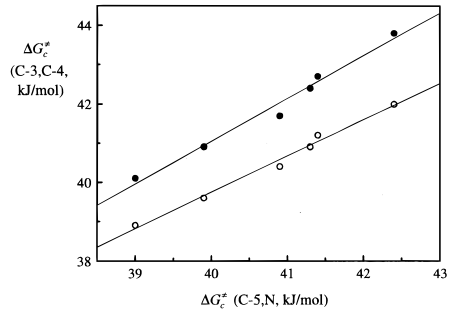


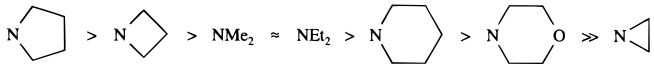

**Figure 3.** Correlations of free energies of activation of the C-3,C-4 and C-5,N rotation in compounds **4** (●, *s-trans* → *s-cis*; ○, *s-cis* → *s-trans*).

of C-4,C-5 rotation observed with increasing donor character of the *para*-phenyl substituent X are in agreement with the findings for compounds **3**[6] and opposite to the increase in the C-3,C-4 barriers in **4** and, therefore, also confirm the assignments made.

The C-2,C-3 rotation process of **4** could be observed from the dynamic $^{13}C$ NMR spectra on the symmetric exchange of cyano groups. In non-polar solvents at room temperature, there was a splitting of the CN signals, but in dimethylformamide and methanol averaged signals were observed. The $\Delta G_c^{\neq}$ of rotation was determined for **4d** to be 63.0 kJ mol$^{-1}$ (Table 5). This relatively high value should be attributed to the low stabilizing capacity of the cyano groups of the transition state. However, compared with **3d**, in which no coalescence could be found up to 453 K,[6] this means a significant decrease in the barrier.

The influence of the solvent on the energy barriers of the other bonds can also be seen for **4d** (Table 5) which was measured in $CD_2Cl_2$ and THF-$d_8$ solution. In the less polar THF-$d_8$, lower $\Delta G_c^{\neq}$ values for the C-3,C-4 and C-5,N rotations were obtained, whereas those of the C-4,C-5 rotation were raised. These results are in agreement with the concept of a polar mechanism assumed for the observed dynamic processes and confirm, in the same way as the effects of substituents do, the assignment of the lineshape alterations to these processes.

**Compounds 5.** In the dynamic $^1H$ NMR spectra of compounds **5** (Table 6), the processes lead to partly superimposed signals. This concerns particularly the signals of the amino groups and their evaluation regarding the C-5,N rotation. On cooling the samples of **5a–d**, first a splitting of the $NCH_2$ signal into two signals of the same population was observed. A large signal difference $\Delta\nu_c$ and a strong high-field shift of the signals were noticeable on further cooling. The C-5,N rotation could be clearly assigned at lower temperatures and showed, including **5f** and **4d**, a gradation comparable to the C-3, C-4 rotation, which was also found for compounds **4**. Therefore, the behaviour described above indicates an exchange process for the amino groups, one of which is situated in the anisotropy cone of the phenyl ring. The same seems to be true for **5f**, although at a lower temperature, whereas for all compounds **4** there was no such additional splitting.




**Scheme 7**

The other rotation processes described for **4** can also be assigned for the compounds **5**. The order of $\Delta G_c^{\neq}$ for **5** corresponds to the gradation of the donor strength of the amino groups predicted from the NMR chemical shifts (Scheme 7). This series was also found in the investigations of the push–pull butadienes **2**.[1]

It is interesting to consider more closely the butadienes **5a** and **c**. The stronger donor capacity of the pyrrolidino than the morpholino group causes a lowering of the barriers to rotation about the C-2,C-3 and C-4,C-5 bonds and an increase in the C-3,C-4 and C-5,N rotation barriers. This alternating effect on the bond system is a feature for the push–pull character of the aminobutadienes. The $\Delta G_c^{\neq}$ values of the dimethylamino compound **4d** lie between those of **5a** and **c**, which also correspond to the $^{13}C$ and $^{15}N$ NMR chemical shifts.

In view of the NMR chemical shifts (see Table 3), for the aziridinyl butadiene **5e** donor–acceptor interactions were expected in the range between **3d** and the other butadienes **5**. This is confirmed by the dynamic NMR measurements. Signal doublings appear already at room temperature owing to the hindered C-4,C-5 rotation. Because of the instability of **5e** at higher temperatures, converting into a cyclization product, the coalescence point in $CDBr_3$ solution could not be reached. However, the coalescence temperature was estimated for H-4 to be 380 ± 5 K. In addition, some rate constants were determined by CLSA in the temperature range below cyclization using the program DNMR5.[26] Therefore, the barrier to rotation is about 40 kJ mol$^{-1}$ higher than in the other butadienes **5** (Table 6). A drastic decrease in the C-3,C-4 and C-5,N barriers takes place simultaneously, so that no signal broadening could be observed down to 180 K.

## CONCLUSION

$^1H$, $^{13}C$ and $^{15}N$ NMR spectroscopy proved very useful for studying push–pull buta-1,3-dienes with respect to $\pi$-electron distribution, stereochemistry and intramolecular mobility. By means of variable-temperature $^1H$ and $^{13}C$ NMR measurements, several dynamic processes in **4** and **5** are observable, which can be assigned unambiguously to different rotational processes about the partial C,C and C,N double bonds of the buta-1,3-diene system. The sizes of energy barriers, determined by lineshape analysis, and the chemical shifts depend on substituent and solvent effects and can be explained on the basis of the push–pull concept.

Compared with normal substituted buta-1,3-dienes, **4** and **5** are characterized by a marked decrease in the barriers to rotation about the double bonds and an increase in the barriers to rotation about the single bonds.

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