## 161. Push-Pull Butadienes: Evidence for a Possible C—H··S Hydrogen Bond in 4-(Methylthio)-4-nitro-1-(pyrrolidin-1-yl)buta-1,3-diene

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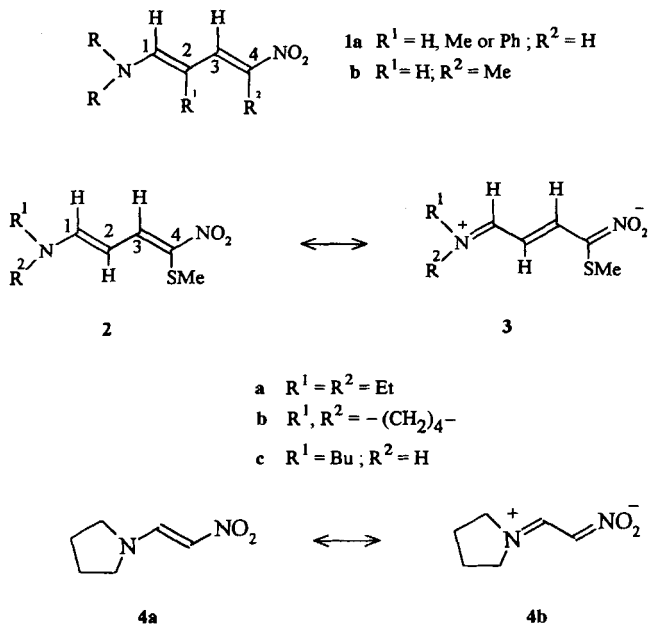
(15. VII. 97)

X-Ray crystal structure of 4-(methylthio)-4-nitro-1-(pyrrolidin-1-yl)buta-1,3-diene (2b)[1]) indicates the presence of a C—H ··· S hydrogen bond. This might also explain the observed downfield shift of this proton in solution.

**1. Introduction.** – 4-Nitrobuta-1,3-dien-1-amines have attracted recent attention as potential optoelectronic materials [1]. Two types of structures are currently accessible through synthesis. Compounds of the type **1a** ($NR_2$ = pyrrolidin-1-yl) were first prepared in 1976 by reaction of aldehydes with 1-(dimethylamino)-2-nitroethylene, followed by treatment with pyrrolidinium acetate [2]. Recently, a closely related compound, 4-methyl-4-nitro-1-(pyrrolidin-1-yl)buta-1,3-diene (**1b**) has been synthesized and its structure and configuration established by X-ray crystallography [1]. The final step in this synthesis involves a 1,6 addition of pyrrolidine to a 1-nitro-4-(phenylthio)buta-1,3-diene, followed by elimination of PhSH. The molecule has been shown to have the (*E, E*)-configuration about the C=C bonds. The C—C bond lengths in the butadiene system (1.37, 1.42, and 1.35 Å for C(1)—C(2), C(2)—C(3), and C(3)—C(4), resp.) clearly indicate the existence of extended conjugation in the push-pull system. The second type of 1-amino-4-nitrobutadiene reported in the literature arises by an extremely facile ring opening of 2-nitrothiophene brought about by *sec*-amines [3]. Subsequent methylation of the thiolate results in compounds such as **2a**. In this case, the configuration about the C=C bonds (*E, Z*) has been established mainly by ${}^1$H-NMR data. While going through the ${}^1$H-NMR data, we were intrigued by one puzzling feature: whereas H—C(2) in **1b** resonates at 4.99 ppm, the corresponding signal for **2a** occurs far downfield at 5.72 ppm. We have undertaken the present study in order to explore the possible reasons for, and consequences of this unexpected downfield shift of H—C(2) in **2**.

**2. Results and Discussion.** – *Synthesis.* Reaction of 2-nitrothiophene with pyrrolidine in the presence of $AgNO_3$ in EtOH at 0° for 10 days gave a silver salt which was methylated by MeI to give **2b** in 52% yield. The butylamino compound **2c** could be prepared in 15% yield from **2b** by transamination.

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[1])   The C-atoms of the butadiene chain have been numbered as shown in **1** and **2**. These numbers have been retained throughout the discussion for the sake of clarity and consistency.

1a  R$^1$ = H, Me or Ph ; R$^2$ = H
 b  R$^1$ = H; R$^2$ = Me

2                              3

a  R$^1$ = R$^2$ = Et
b  R$^1$, R$^2$ = –(CH$_2$)$_4$–
c  R$^1$ = Bu ; R$^2$ = H

4a                           4b

*¹H-NMR Data.* The ¹H-NMR signals of **2b** matched well with those reported for the diethylamino compound **2a** [3]; H–C(2) was seen at 5.6 ppm as *triplet*. In the butylamino analog **2c**, this proton resonated even further downfield at 5.8 ppm.

During our early investigations on 1-nitro-2-(pyrrolidin-1-yl)ethylene (**4a**) and related compounds, we had shown that the strong contribution of the iminium-nitronate structure **4b** resulted in magnetic non-equivalence of the α-CH$_2$ protons of the pyrrolidine [4]. The compound **2b** similarly exhibits magnetic nonequivalence of the α-CH$_2$ groups both in ¹H- and ¹³C-NMR spectra (¹H: 3.40, 3.60 ppm; ¹³C: 47.33, 52.74 ppm). This clearly indicates extended conjugation over the entire molecule as in **3b**.

*Reactivity at C(2).* The chemical shift of H–C(2) in **2b** clearly indicates that there is no additional enaminic electron density at C(2). This was confirmed in two ways. Addition of D$_2$O to the CDCl$_3$ solution of **2b** did not result in any exchange of H–C(2). Furthermore, the compound was recovered unreacted after treatment with the moderately strong electrophile, MeNCS (toluene, reflux, 24 h). We had shown earlier that this is a diagnostic test for enaminic reactivity in nitrovinylamines [5].

*Crystal Structure of **2b**²).* The X-ray crystal structure of compound **2b** is shown in *Fig. 1*, and the selected bond lengths and bond angles are given in *Table 1*. As can be seen from *Table 2*, the central butadiene moiety is essentially coplanar with the terminal N,N-dialkylamino and NO$_2$ substituents. However, the Me–S bond is nearly perpendicular to the above plane. The C–C and C=C bond lengths in this push-pull diene system

have become almost equivalent ($\sim 1.38$ Å) suggesting a large delocalization of the $\pi$-electron cloud. This is also manifested by a shorter (1.308 Å) N–C distance at the amino end relative to the value (1.323 Å) found in the closely related compound **2a** [1]. A common feature present in both these molecules is the smaller bond angle at C(3) ($\sim 120°$) as compared to the two flanking angles at C(2) and C(4) ($\sim 127°$)[3]).
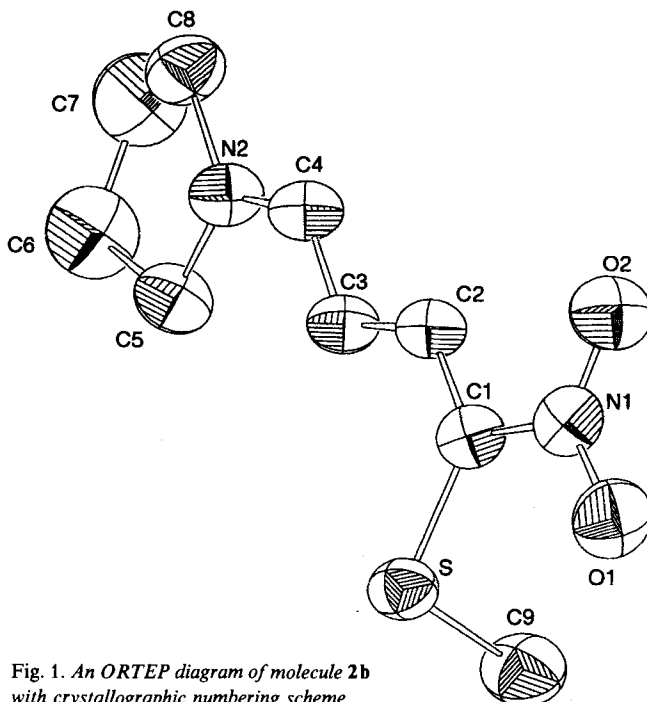
Fig. 1. *An ORTEP diagram of molecule* **2b** *with crystallographic numbering scheme*

*Intramolecular CH · · · S Interaction.* The structure shows a close contact between S and H–C(3) (*Table 3*). However, more than the distance it is the spatial disposition of H–C(3) relative to the thioether plane that is revealing. According to *Rosenfield et al.* [6], in compounds containing divalent S (bonded to two ligands, Y and Z), there may exist interactions such that a group with electrophile character approaches S roughly 20° from the perpendicular to the plane through atoms Y–S–Z. This is indeed the case here; the ethylenic proton H–C(3), acting as an electrophile, interacts in a very similar fashion (the above-mentioned angle is 27°) with the S-atom (*Table 3* and *Fig. 2*). The stability resulting from the positioning of the proton along a S lone-pair orbital [6] may be responsible for the near perpendicular orientation of the thioether group with respect to the rest of the molecule. (For yet another favorable interaction that this particular orientation offers, see the discussion below.) Because of the attractive nature, this may constitute an interesting example of the H-bonding, even though a C(3)–H · · · S angle of 105°, significantly differing from the linear direction, is not deemed to constitute a strong interaction

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[3])   Atom numbering as in *Fig. 1.*

Table 1. *Selected Bond Lengths [Å] and Angles [°] for Compound* **2b**

| Bond lenghts | | | |
|---|---|---|---|
| S–C(1) | 1.746(3) | N(2)–C(5) | 1.472(3) |
| S–C(9) | 1.792(3) | C(1)–C(2) | 1.371(3) |
| O(1)–N(1) | 1.249(3) | C(2)–C(3) | 1.380(4) |
| O(2)–N(1) | 1.236(3) | C(3)–C(4) | 1.380(4) |
| N(1)–C(1) | 1.421(3) | C(5)–C(6) | 1.517(4) |
| N(2)–C(4) | 1.308(3) | C(6)–C(7) | 1.479(6) |
| N(2)–C(8) | 1.469(3) | C(7)–C(8) | 1.476(5) |
| **Bond angles** | | | |
| C(1)–S–C(9) | 102.2(1) | N(1)–C(1)–S | 118.2(2) |
| O(2)–N(1)–O(1) | 120.7(2) | C(1)–C(2)–C(3) | 126.9(2) |
| O(2)–N(1)–C(1) | 120.1(2) | C(4)–C(3)–C(2) | 120.9(2) |
| O(1)–N(1)–C(1) | 119.2(2) | N(2)–C(4)–C(3) | 126.2(2) |
| C(4)–N(2)–C(8) | 124.9(2) | N(2)–C(5)–C(6) | 103.9(2) |
| C(4)–N(2)–C(5) | 123.9(2) | C(7)–C(6)–C(5) | 105.6(3) |
| C(8)–N(2)–C(5) | 110.9(2) | C(8)–C(7)–C(6) | 106.2(3) |
| C(2)–C(1)–N(1) | 117.9(2) | N(2)–C(8)–C(7) | 104.1(3) |
| C(2)–C(1)–S | 123.8(2) | | |

Table 2. *Angle between Various Atomic Planes in* **2b**

| Planes[a]) | Angle [°] |
|---|---|
| Amino/butadiene | 8.9(4) |
| Nitro/butadiene | 5.0(4) |
| Thioether/butadiene | 78.9(1) |
| Nitro/amino | 13.4(4) |
| Nitro/thioether | 74.8(2) |

[a]) Atoms used to define various planar groups are: butadiene: C(1), C(2), C(3), C(4); amino: C(5), N(2), C(8); nitro: N(1), O(1), O(2); thioether: C(1), S, C(9).

[7]. It may be that as long as the proton is directed towards a more electron-dense (like the lone-pair) part of the acceptor atom, considerable energy is to be gained from even a nonlinear H-bonding geometry.

*Intermolecular CH · · · O and S · · · O Interactions.* The two shortest contacts stabilizing the crystal lattice involve the O-atoms of the $NO_2$ group (*Table 4*). The CH · · · O interaction is interesting as it shows that the C–H bond can be lengthened by its participation in a H-bond as has also been observed for the O–H · · · O H-bonds [8]. The C(4)–H bond length (0.94 Å) is longer by *ca.* 0.08 Å compared to the other two C–H bonds with no comparable intermolecular interaction. The fact that all the H-positions have been obtained from the difference *Fourier* map and ethylene H-atoms have been subjected to refinement confers a degree of confidence to these statements.

The already alluded work of *Rosenfield et al.* [6] is useful in understanding the geometry of the other crystal contact *viz.,* between S- and O-atoms. They had observed that the preferred direction of interaction of a nucleophile with the S-atom in the group

Fig. 2. *Spherical polar coordinates specifying the direction of* $S \cdots H-C(3)$ *are defined relative to the axial system, with S as the origin z, normal to the plane defined by* $C(1)$, $S$, *and* $C(9)$; *x, bisector of the angle* $C(1)-S-C(9)$, *and the y-axis going in the direction of* $C(1)$. *The polar angle* $\theta$ $(0 \leq \theta \leq 180°)$ *is the angle made by the* $S \cdots H-C(3)$ *vector with the positive z direction; the positive direction of* $\phi$ *is as shown. In the text, two such angles have also been defined for* O(2), *which shows an intermolecular contact with the S-atom.*
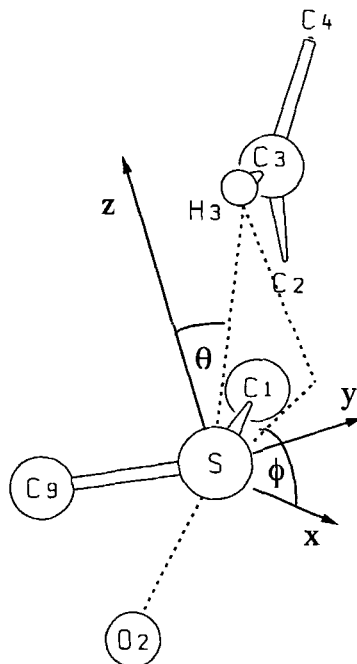
Table 3. *Geometric Parameters Involving the Interaction between the S- and the H-Atom,* $H-C(3)$ *in* **2b**

| Atoms | Length [Å] | Polar angles[a]) | |
|---|---|---|---|
| $C(3)-H \cdots S$ | 2.86(3) | $\theta$ | 26.7(1) |
| $C(3) \cdots S$ | 3.192(3) | $\phi$ | 111.7(1) |
| | Angle [°] | | |
| $C(3)-H \cdots S$ | 105.1(6) | | |
| $C(1)-S \cdots H-C(3)$ | 64.6(6) | | |
| $C(9)-S \cdots H-C(3)$ | 102.8(6) | | |

[a]) Angles $\theta$ and $\phi$ are defined in *Fig. 2*.

Table 4. *Distances [Å] and Angles [°] Involving Close Intermolecular Interactions in the Crystal Structure of* **2b**

| CH $\cdots$ O Interaction[a]) | | S $\cdots$ O Interaction[a]) | |
|---|---|---|---|
| $C(4) \cdots O(1)$ | 3.240(3) | $S \cdots O(2)$ | 3.340(2) |
| $C(4)-H \cdots O(1)$ | 2.41(3) | $\theta$[b]) | 97.3(1) |
| $C(4)-H \cdots O(1)$ | 147(2) | $\phi$[b]) | $-53.2(1)$ |

[a]) Symmetry operators to be applied to O(1): $2 - x$, $0.5 + y$, $0.5 - z$; O(2): $2 - x$, $-0.5 + y$, $0.5 - z$.
[b]) $\theta$ and $\phi$ angles are defined in *Fig. 2*.

$Y-S-Z$ is along the extension of the $S-Y$ or $S-Z$ bond. This translates to a value of $\theta \approx 90°$ and $\phi \approx \pm 60°$ (*Fig. 2*) for the O-atom, O(2), which, with its partial negative charge, can behave like a nucleophile. This is indeed what we observe (*Table 4*).

In summary, the present crystallographic investigation has identified a system where both the molecular and the crystal structures have been modulated so as to satisfy the special feature of the S atom, *viz.*, its nucleophilic, as well as electrophilic nature in making nonbonded contacts.

**Conclusion.** – The explanation for the downfield shift of H−C(2) in **2b** relative to that in **1b** perhaps lies in the spatial proximity of this proton in **2b** to the S-atom; in the solid state, the orientation of this proton leads to a C−H ⋯ S H-bond as revealed by the X-ray analysis. We believe that this situation also exists in solution, thereby leading to the observed downfield shift of H−C(2) in the ¹H-NMR spectrum. If this were indeed the case, this would be another example of the manifestation of a weak attractive force *in solution* involving the S-atom.

## Experimental Part

*General.* M.p.: with a microsope hot-stage apparatus, uncorrected. IR spectra: *Perkin-Elmer-Infracord* spectrometer. ¹H- and ¹³C-NMR spectra: *Bruker-Ac-200* or *Bruker-MSL-300* instrument in CDCl₃ soln. with TMS as internal standard, coupling constants *J* are given in Hz. MS: a *Finnigan-MAT-102B* spectrometer. Microanalyses were performed at the Organic Chemistry Division, NCL.

*4-(Methylthio)-4-nitro-1-(pyrrolidino-1-yl)buta-1,3-diene* (**2b**). Pyrrolidine (16.89 g, 238 mmol) was added dropwise to a stirred soln. of AgNO₃ (4.48 g, 28.52 mmol) in EtOH (130 ml). A small amount of black precipitate was formed, which was filtered off. To the filtrate 2-nitrothiophene (3.5 g, 27.13 mmol) in EtOH (35 ml) was added. The dark-red colored soln. was kept at 0° for *ca.* 10 d. The red-colored precipitate (silver salt) was filtered, washed with EtOH and Et₂O, and dried. To the dried silver salt excess MeI (15 ml) was added and the mixture stirred at 30° for 30 min. It was then extracted with acetone, the acetone layer was concentrated and the solid purified by silica-gel column chromatography using petroleum ether and AcOEt to give **2b** (52%). Dark-red crystals. M.p. 137° (AcOEt). IR (CHCl₃): 1600, 1560, 1400, 1260, 1200. ¹H-NMR (CDCl₃): 2.05 (*m*, 2 CH₂); 2.25 (*s*, MeS); 3.4 (*t*, CH₂); 3.6 (*t*, CH₂); 5.6 (*t*, *J* = 12.3, =CH); 7.35 (*d*, *J* = 12.3, =CH); 8.25 (*d*, *J* = 12.3, = CH). ¹³C-NMR (CDCl₃): 16.95; 24.64; 43.33; 52.74; 98.08; 128.84; 148.93; 153.07. MS: 214 (*M*⁺), 120 (100), 93, 84, 80, 76, 70, 55. Anal. calc. for C₉H₁₄N₂O₂S: C 50.45, H 6.58, N 13.07; found: C 50.84, H 7.08, N 13.17.

*1-(Butylamino)-4-(methylthio)-4-nitrobuta-1,3-diene* (**2c**). The pyrrolidinyl derivative **2b** (214 mg, 1 mmol) was taken in dry MeOH (5 ml) and to that was added BuNH₂ (183 mg, 2.5 mmol) and a catal. amount of TsOH. The mixture was refluxed for 30 h, the solvent removed and the product purified by silica-gel column chromatography using petroleum ether and AcOEt to give **2c** (15%). Red-colored gum. IR (CHCl₃): 1180, 1550, 1600, 3300. ¹H-NMR (CDCl₃): 1.0 (*t*, Me); 1.45 (*m*, CH₂); 1.65 (*m*, CH₂); 2.25 (*s*, Me); 3.3 (*t*, CH₂); 5.8 (*t*, *J* = 12.6, = CH); 6.1 (br. *s*, NH, exchanged with D₂O); 7.25 (*m*, =CH); 8.3 (*d*, *J* = 12.2, =CH). MS: 216 (*M*⁺), 120 (100), 93, 84, 80, 76, 70.

*Crystallographic Analysis of* **2b**. *Crystal Data.* The reflection data collected were reduced using NRCVAX program [9]. The structure was solved by direct method using the SHELXS-86 program [10] and refined by full-matrix least-squares method on *F*². Anisotropic thermal parameters were used for refinement of non-H-atoms. All H-positions were obtained from the difference *Fourier* map. The coordinates and the isotropic temp. factors of the three ethylene H-atoms were refined, but the others were held fixed. These calculations were done with the PC version of SHELXL-93 [11] using standard atomic scattering factors from '*International Tables for Crystallography*'.

Table 5. *Crystal Data and Refinement for* **2b**

| | | |
|---|---|---|
| Systematic name | 4-(Methylthio)-4-nitro-1-(pyrrolidin-1-yl)buta-1,3-diene | |
| Source of material | Synthetic | |
| Solvent for crystallization | AcOEt | |
| Chemical formula | $C_9H_{14}N_2O_2S$ | |
| Formula weight | 214.28 | |
| Unit cell dimensions | $a = 9.232(2)$ Å $\alpha = 90.0(0)°$ | |
| | $b = 12.083(2)$ Å $\beta = 109.79(2)°$ | |
| | $c = 10.319(2)$ Å $\gamma = 90.0(0)°$ | |
| Volume | $1083.1(4)$ Å$^3$ | |
| Crystal system | Monoclinic | |
| Space group | $P\,2_1/c$ | |
| No. of molecules per unit cell | 4 | |
| Diffractometer used | *Enraf-Nonius CAD-4* | |
| Radiation | $MoK_\alpha$ | |
| Wavelength | 0.70930 Å | |
| Temp. | 293(2) K | |
| Pressure | 1 Atm | |
| Calculated density | 1.314 Mgm$^{-3}$ | |
| Linear absorption coefficient | 0.276 mm$^{-1}$ | |
| Method of measuring intensities | $\omega-2\theta$ | |
| Maximum $\theta$ reached during intensity measurements | 23.46° | |
| $F(000)$ | 456 | |
| Type of absortion correction applied | None | |
| Method used to solve structure | Direct method | |
| to refine structure | Full matrix least-squares on $F^2$ | |
| H treatment | Differnce *Fourier* | |
| No of independent reflections | 1602 | |
| of observed reflections | 1390 | |
| Reflections observed criterion | $I > 2\sigma(I)$ | |
| No of parameters refined | 140 | |
| Final values of $R$ | $R1 = 0.0516$, $wR2 = 0.1437$ for $I > 2\sigma(I)$ | |
| | $R1 = 0.0571$, $wR2 = 0.1496$ for all data | |
| | $w = 1/[\sigma^2 F_o^2 + (0.1138P)^2 + 0.2877P]$, | |
| | where $P = (F_o^2 + 2F_c^2)/3$ | |
| Goodness of fit | 1.073 for observed data | |
| | 1.035 for all data | |
| Extinction coefficient | 0.012(4) | |
| Max. positive and negative densities | 0.328 and $-0.395$ e $\cdot$ Å$^{-3}$ | |
| All computer programs used | NRCVAX (PC Version), SHELXS-86, | |
| | SHELXL-93, ORTEP[12] | |

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