

ω scans
Absorption correction: none
4333 measured reflections
4126 independent reflections
1983 reflections with
 $I > 2\sigma(I)$

$h = -11 \rightarrow 11$
 $k = -11 \rightarrow 12$
 $l = -14 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.125$
 $S = 0.994$
4126 reflections
280 parameters
H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.0391P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.167 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.169 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å , $^\circ$)

O1—N	1.431 (2)	C2—C3	1.538 (3)
O1—C3	1.466 (3)	C3—C4	1.485 (3)
N—C22	1.417 (3)	C4—C5	1.324 (3)
N—C1	1.465 (3)	C5—C6	1.454 (3)
C1—C2	1.535 (3)	C6—C7	1.342 (3)
C2—C6	1.516 (3)	C7—C8	1.452 (4)
N—O1—C3	106.81 (17)	O1—C3—C4	114.7 (2)
C22—N—O1	114.17 (18)	O1—C3—C2	106.19 (19)
C22—N—C1	122.45 (19)	C4—C3—C2	104.8 (2)
O1—N—C1	103.85 (17)	C5—C4—C3	111.3 (2)
N—C1—C15	107.92 (18)	C4—C5—C6	112.7 (3)
N—C1—C2	105.82 (18)	C7—C6—C5	124.6 (2)
C15—C1—C2	112.86 (19)	C7—C6—C2	129.3 (2)
C6—C2—C1	115.5 (2)	C5—C6—C2	106.1 (2)
C6—C2—C3	105.08 (19)	C6—C7—C8	130.9 (2)
C1—C2—C3	102.43 (19)		

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN11/82* (Main *et al.*, 1982). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP3* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1001). Services for accessing these data are described at the back of the journal.

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Monomeric pNBS: Bis(*p*-nitrobenzenesulfonate) of 2,4-Hexadiyne

MARCEL BERTAULT, JACKY EVEN AND LOIC TOUPET

Groupe Matière Condensée et Matériaux, UMR 6626 au CNRS, Université de Rennes I, Campus de Beaulieu, 35042 Rennes CEDEX, France. E-mail: toupet@univ-rennes1.fr

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Abstract

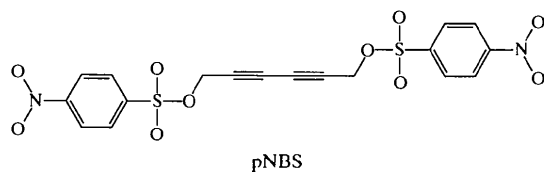
The title compound, 2,4-hexadiyne-1,6-diyl bis(*p*-nitrobenzenesulfonate), (pNBS), C₁₈H₁₂N₂O₁₀S₂, is a symmetrical di-*para*-substituted diacetylene $R-C\equiv C-C\equiv C-R$, where R is $-CH_2-O-SO_2-C_6H_4-NO_2$. In this compound, the volume of the NO₂ group is 23.0 Å³, almost equal to that of a CH₃ group (23.5 Å³) in the well known polymerizable symmetrical diacetylene, 2,4-hexadiyne-1,6-diyl bis(*p*-toluenesulfonate) (pTS). pNBS, however, crystallizes in an unreactive monomeric form.

Comment

Some diacetylenes ($R-C\equiv C-C\equiv C-R$) polymerize in the solid state (Wegner, 1969). The polymerization process conforms to the topochemical principle enunciated by Schmidt (1971), in which the crystal structure of the reactant completely controls the nature of the product formed. For the diacetylenes, the structure of the monomer completely defines the reactivity, but no general rules are known which predict a favourable monomeric structure (Enkelmann, 1984). We recently became interested in diacetylenes of the structural type 2,4-hexadiyne-1,6-diyl bis(*p*-toluenesulfonate) (pTS) (Aimé *et al.*, 1982, 1988; Even *et al.*, 1994, 1995).

For pTS-type compounds, where R is $-CH_2-O-SO_2-C_6H_4-CH_3$, we wanted to compare the effects of various *para* substituents on the benzene ring on the polymerization reactivity of the compounds. A systematic study of this substitution is available in the literature (Ando *et al.*, 1979). By considering substituents with increasing volume (Kitaigorodsky, 1973), one can begin with the unsubstituted BSHD diacetylene; here R is $-CH_2-O-SO_2-C_6H_5$ and the molecule polymerizes (Ando *et al.*, 1979, 1985). The fluoro-substituted compound, pFBS, where R is $CH_2-O-SO_2-C_6H_4-F$ (Aimé *et al.*, 1988; Yee, 1979), is also reactive. The chloro-substituted compound, pCBS, has both a reactive and an unreactive form (Ando *et al.*, 1979; Mayerle & Clarke, 1978). The methyl-substituted compound, pTS, where R is $-CH_2-O-SO_2-C_6H_4-CH_3$, polymerizes rapidly. The bromo-substituted compound, pBBS, has both a reactive and

an unreactive form (Ando *et al.*, 1979; Williams *et al.*, 1982). The methoxy-substituted compound, pMBS, where R is $-\text{CH}_2-\text{O}-\text{SO}_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_3$, also has both a reactive and an unreactive form (Ando *et al.*, 1979; Fisher *et al.*, 1979). The structures of the unreactive forms of pCBS, pBBS and pMBS are known, but those of the reactive forms are unknown, probably because these diacetylenes polymerize upon X-ray irradiation. Neutron diffraction has enabled the accurate determination of the structures of the reactive pTS and pFBS monomers. The slow polymerization rate of BSHD also provided the opportunity to perform a structure determination by X-ray crystallography. We decided to synthesize a *p*-nitro-substituted compound, pNBS, which is similar to pTS, since all the previous examples show at least one polymerizable form. It must be pointed out that the volume increment of the NO_2 group, 23.0 \AA^3 (Kitaigorodsky, 1973), is very near to that of the CH_3 group (pTS), which is 23.5 \AA^3 ; the other volume increments (halide substituents) are, respectively, 9.6 (F), 19.9 (Cl) and 26.0 \AA^3 (Br).



The molecular conformation of a pNBS molecule in the crystal is shown in Fig. 1. A projection of the unit cell of the pNBS crystallographic structure along the $[101]$ direction is shown in Fig. 2. Maximal reactivity is observed for the solid-state polymerization

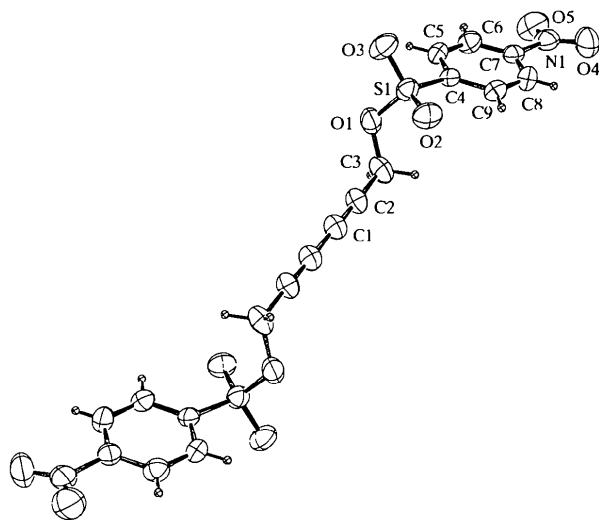


Fig. 1. The molecular structure of pNBS, showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Atom numbering takes into account the symmetry of the molecule.

of diacetylenes when parallel diacetylene backbones of adjacent molecules are separated by a distance of about 5 \AA (Enkelmann, 1984). Such packing is not observed for adjacent molecules in the pNBS structure, where the distance is much larger (Fig. 2); for example, the distance between pNBS molecules along the b axis is equal to $10.288(4) \text{ \AA}$. The packing in the pNBS structure is completely different from that of pTS (Aimé *et al.*, 1982); it is characterized by contacts between the side groups of one molecule and the diacetylene backbone of an adjacent one. Indeed, the smallest intermolecular $\text{O}_{\text{nitro}} \cdots \text{C}$ distance is $3.272(6) \text{ \AA}$ and the smallest $\text{N} \cdots \text{C}$ distance is $3.299(6) \text{ \AA}$, which correspond, in both cases, to the sum of the van der Waals radii (Kitaigorodsky, 1973).

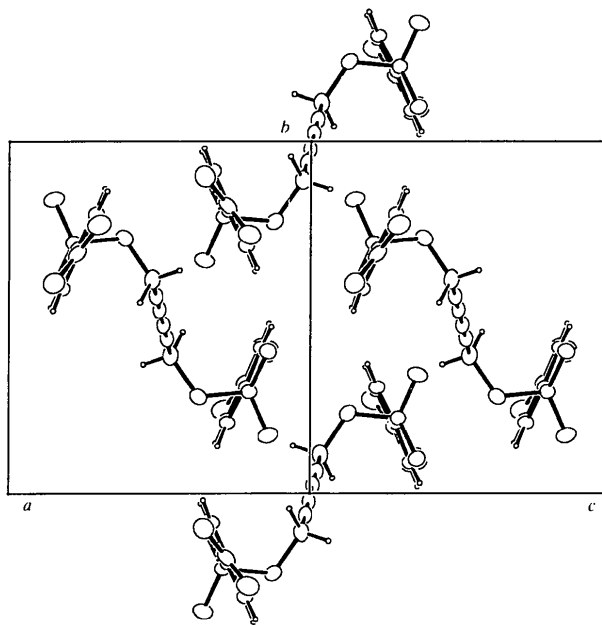


Fig. 2. A projection of the unit cell of the pNBS structure down the $[101]$ direction showing the packing of adjacent molecules.

Experimental

2,4-Hexadiyne-1,6-diyl bis(*p*-nitrobenzenesulfonate) (pNBS) was prepared at about 278 K by the reaction of *p*-nitrobenzenesulfonyl chloride with 2,4-hexadiyne-1,6-diol in acetone; at the same time, a concentrated aqueous solution of potassium hydroxide was added dropwise to the mixture. We used several minor modifications of the method reported by Wegner (1971) for the analogous ditosylate derivative, pTS. Recrystallization from acetone gave a yellow-brown material which was characterized by NMR. Single crystals suitable for the X-ray study were obtained by slow evaporation of an acetone solution at room temperature. No solid-state reaction in the form of polymerization was observed during crystallization or the X-ray study, nor after several hours in the drying oven at 353 K.

Crystal data

C₁₈H₁₂N₂O₁₀S₂M_r = 480.43

Monoclinic

P2₁/c

a = 10.510 (3) Å

b = 10.288 (4) Å

c = 10.227 (3) Å

β = 117.60 (2)°

V = 980.0 (6) Å³

Z = 2

D_x = 1.63 Mg m⁻³D_m not measured

Data collection

Enraf-Nonius CAD-4
diffractometer

ω scans

Absorption correction: none

1835 measured reflections

1728 independent reflections

1053 reflections with

I > 2σ(I)

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 8.0–13.0°

μ = 0.335 mm⁻¹

T = 294 K

Prism

0.35 × 0.35 × 0.20 mm

White

R_{int} = 0.063θ_{max} = 25°

h = -12 → 12

k = 0 → 12

l = 0 → 12

3 standard reflections

frequency: 60 min

intensity decay: 0.60%

Refinement

Refinement on F²

R(F) = 0.034

wR(F²) = 0.077

S = 1.066

1728 reflections

163 parameters

Only coordinates of H atoms
refined $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.3497P]$ where $P = (F_o^2 + 2F_c^2)/3$ (Δ/σ)_{max} < 0.001Δρ_{max} = 0.221 e Å⁻³Δρ_{min} = -0.243 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—O1	1.568 (3)	N1—C7	1.471 (6)
S1—C4	1.763 (6)	C1—C2	1.185 (5)
O1—C3	1.452 (4)	C1—C1'	1.387 (7)
O4—N1	1.216 (4)	C2—C3	1.450 (5)
O5—N1	1.218 (4)		
O1—S1—C4	103.55 (14)	O5—N1—C7	117.9 (3)
C3—O1—S1	118.0 (2)	C2—C1—C1'	179.5 (4)
O4—N1—O5	124.2 (3)	C1—C2—C3	178.8 (3)
O4—N1—C7	117.9 (3)	C2—C3—O1	110.7 (3)

Symmetry code: (i) 1 - x, -y, 1 - z.

Backgrounds were obtained from analysis of the scan profile (Blessing *et al.*, 1974).Data collection: CAD-4 Operations Manual (Enraf-Nonius, 1977). Cell refinement: CAD-4 Operations Manual. Data reduction: PROCESS in MolEN (Fair, 1990). Program(s) used to solve structure: SIR (Burla *et al.*, 1989). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: BTABLE PTABLE CIF IN in MolEN.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1048). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1030–1033**(5aR,9aR)-2,4-Dimethyl-5a,6,7,8,9,9a-hexahydro-1H-1,5-benzodiazepine**

RICHARD F. JORDAN, DAVID G. BLACK AND DALE C. SWENSON

Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA. E-mail: dale-swenson@uiowa.edu

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Abstract

The title compound, C₁₁H₁₈N₂, packs in the solid state with one molecule in the asymmetric unit, but with the chiral molecule disordered over two orientations related by twofold rotation. Thus, the molecule is the average of these two orientations, with the amine H