

Spek, A. L. (1994). *PLUTON. Molecular Graphics Program*. University of Utrecht, The Netherlands.  
 Takusagawa, F., Hirotsu, K. & Shimada, A. (1973). *Bull. Chem. Soc. Jpn.*, **46**, 2020–2027.

*Acta Cryst.* (1998). **C54**, 1027–1028

### 4-Benzoyl-6-(4-methoxybenzylidene)-3-phenyl-2-oxa-3-azabicyclo[3.3.0]oct-7-ene

MAREK M. KUBICKI,<sup>a</sup> OLIVIER BLACQUE,<sup>a</sup> FRANCIS DJAPA,<sup>b</sup> KABULA CIAMALA<sup>b</sup> AND JOËL VEBREL<sup>b</sup>

<sup>a</sup>Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (UMR 5632), Université de Bourgogne, Faculté des Sciences, 6 boulevard Gabriel, 21000 Dijon, France, and <sup>b</sup>Laboratoire de Chimie Organique, Université de Franche-Comté, 16 Route de Gray, La Bouloie, 25030 Besançon, France. E-mail: marek.kubicki@u-bourgogne.fr

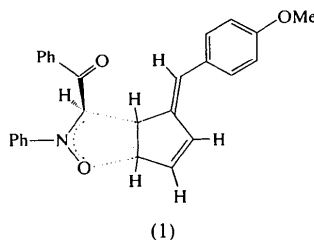
(Received 20 November 1997; accepted 30 January 1998)

#### Abstract

The title compound, C<sub>27</sub>H<sub>23</sub>NO<sub>3</sub>, consists of a fulvene–1,3-dipolar-nitrone adduct with a five-membered C<sub>3</sub>NO saturated heterocycle.

#### Comment

The 1,3-dipolarophilic reactivity of fulvenes towards some 1,3-dipoles has been studied for many years (Alder *et al.*, 1961; Houk & Luskus, 1970; Caramella *et al.*, 1971) but, to the best of our knowledge, nitrones have never been used as 1,3-dipole targets. The structure of the title compound, (1), shows that the fulvene–1,3-dipolar-nitrone reaction proceeds through the usual pathway. Cycloaddition involves one of the two fulvenic



double bonds (C2=C3 and C4=C5). The second one, equal to 1.324 (3) Å in (1), is not affected by cycloaddition. The central saturated cycle is puckered and exhibits a 'boat-like' geometry over the planar C1–C2–C3–O1 unit. The dihedral angles involving this unit with the O1–N–C1 and C2–C6 planes are equal to 37.1 (2) and 58.7 (2)°, respectively. The fulvene-

derived fragment in (1) remains almost planar, with the dihedral angle between the C2–C6 and C8–C13 planes equal to 6.6 (1)°. A perspective view of the title molecule is shown in Fig. 1.

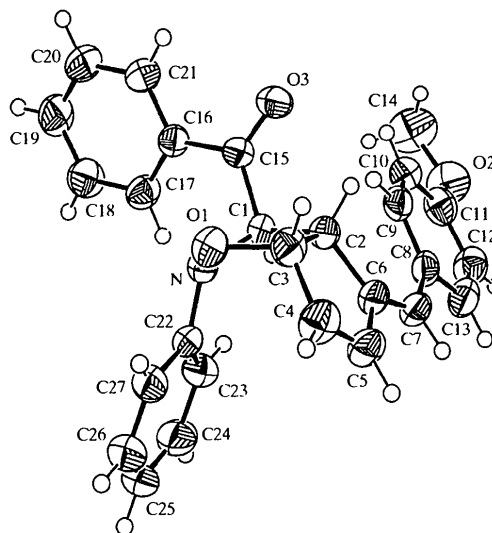


Fig. 1. View of the molecular structure of (1) showing 50% probability displacement ellipsoids.

#### Experimental

In the course of our studies on 1,3-dipolar cycloadditions, the reaction involving a fulvene and a nitrone has been carried out. A mixture of 3 mmol of 6-*p*-anisylpentafulvene and 5 mmol of nitrone were refluxed for 15 h in THF. After evaporation of the solvent, the crude oil, containing formally at least eight regio- and stereoisomers, was dissolved in ethanol and the major product, (1), was separated by thin-layer chromatography on silica gel (57% yield). Crystals of (1) suitable for X-ray measurements were grown from ethanol.

#### Crystal data

C<sub>27</sub>H<sub>23</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 409.46  
 Triclinic  
*P* $\bar{1}$   
*a* = 9.542 (5) Å  
*b* = 10.327 (6) Å  
*c* = 11.857 (9) Å  
 $\alpha$  = 114.41 (5)°  
 $\beta$  = 90.70 (5)°  
 $\gamma$  = 96.61 (5)°  
*V* = 1054.5 (11) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.290 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 8.74–18.07°  
 $\mu$  = 0.084 mm<sup>-1</sup>  
*T* = 296 (1) K  
 Irregular  
 0.25 × 0.15 × 0.15 mm  
 Pale yellow

Data collection  
 Enraf–Nonius CAD-4 diffractometer

*R*<sub>int</sub> = 0.030  
 $\theta$ <sub>max</sub> = 26.31°

$\omega$  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 ( $\text{Å}$ ,  $^\circ$ )

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.

### References

- Alder, K., Braden, R. & Floch, H. (1961). *Chem. Ber.* **94**, 456–467.  
 Caramella, P., Frattini, P. & Grünanger, P. (1971). *Tetrahedron Lett.* **41**, 3817–3820.  
 Enraf–Nonius (1992). *CAD-4 EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.  
 Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.  
 Farrugia, L. J. (1997). *ORTEP3*. Version 1.02. University of Glasgow, Scotland.  
 Houk, K. N. & Luskus, L. J. (1970). *Tetrahedron Lett.* **46**, 4029–4031.  
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.  
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

*Acta Cryst.* (1998). **C54**, 1028–1030

## 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*

(Received 6 October 1997; accepted 12 January 1998)

### Abstract

The title compound, 2,4-hexadiyne-1,6-diyl bis(*p*-nitrobenzenesulfonate), (pNBS), C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>, 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 NO<sub>2</sub> group is 23.0 Å<sup>3</sup>, almost equal to that of a CH<sub>3</sub> group (23.5 Å<sup>3</sup>) 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