Journal of the Korean Chemical Society
Vol. 37, No. 3, 1993
Printed in the Republic of Korea

Z-1-에칠-2-니트로-1-부텐일-(4′-메칠)-페닐 슬폰의 구조

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(1992. 8. 5 접수)

Structure of Z-1-Ethyl-2-Nitro-1-Butenyl-(4′-Methyl)-Phenyl Sulfone

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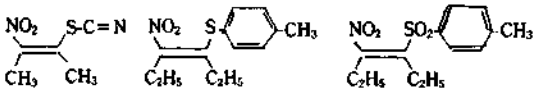
(Received August 5, 1992)

요 약. Z-1-에칠-2-니트로-1-부텐일-(4′-메칠)-페닐 슬폰, $C_{13}H_{17}NO_4S$의 분자량은 283.4으로 $a=12.194(7)$, $b=7.290(4)$, $c=16.532(14)$Å, $\beta=103.4(2)°$, $V=1429.5$ Å^3, $Z=4$, $D_c=1.32$ g·cm^{-3}, λ(Mo $K\alpha$)$=0.71069$ Å, $\mu=2.2$cm^{-1}, $F(000)=600$, $T=298$ K으로 단사정계에 계속하여 $P2_1/c$의 공간군을 갖으며 1762개의 $I>1.0\sigma(I)$인 회절반점에 대하여 $R=0.050$이었다. 분자는 메칠밴젠고리에 결합된 S 원자와 NO_2기에 결합된 "치환된 부탠골격", C-C=C-C으로 이뤄진 *cis*-형의 분자구조를 갖고 있다. 메칠밴젠고리와 치환된 부텐부분은 거의 평면으로 되어 있으며 그들 자신의 분자평면으로 부터의 각각의 최대편차는 밴젠기의 C(1) 원자의 0.018 Å와 NO_2기의 N 원자의 0.045 Å이다. 부탠골격의 평면은 메칠벤젠의 평면과 88.5°를 또 NO_2기와의 평면은 78.6°를 이루고 있다. 부텐평면으로부터의 NO_2기의 회전은 NO_2기가 가지고 있는 공명구조의 기여도를 감소하여 SO_2기의 O(2) 원자와 NO_2기의 O(3) 원자 사이에서 일어나는 반발로 그 거리가 2.8 Å의 예상된 van der Waals 거리보다 긴 2.894 Å로 되어 있다.

ABSTRACT. Z-1-Ethyl-2-nitro-1-butenyl-(4′-methyl)-phenyl sulfone, $C_{13}H_{17}NO_4S$, Mr=293.4, monoclinic space group $P2_1/c$, $a=12.194(7)$, $b=7.290(4)$, $c=16.532(14)$Å, $\beta=103.4(2)°$, $V=1429.5$ Å^3, $Z=4$, $D_c=1.32$ g·cm^{-3}, λ(Mo $K\alpha$)$=0.71069$ Å, $\mu=2.2$ cm^{-1}, $F(000)=600$, $T=298$ K, $R=0.050$ for 1762 unique observed reflections with $I>1.0\sigma(I)$. A molecule has a *cis*-typed molecular structure having the form of "the substituted butene backbone", C-C=C-C, connecting to a sulfur atom with the methylbenzene ring and to a nitro group. The methylbenzene ring and the substituted butene moiety are nearly planar with the maximum deviations from their own molecular planes, 0.018 Å for the C(1) atom of the benzene group and 0.045 Å for the N atom of the NO_2 group, respectively. The angles to the plane of the butene backbone are 88.5° from the plane of the methyl-benzene and 78.6° from the plane of the nitro group. Rotation of the nitro group from the butene plane seems to reduced contribution of resonance structure involving the nitro group, and resultant repulsion between the O(2) atom of SO_2 and the O(3) atom of NO_2 appears to be 2.894 Å longer than an expected van der Waals distance of 2.80 Å.

INTRODUCTION

As part of the studies on substituted butenes, the crystal structure analysis of Z-1-ethyl-2-nitro-1-butenyl-(4'-methyl)-phenyl sulfone (c) was undertaken in order to elucidate the geometry of the skeleton of the butene moiety including the nitro group and the sulfur atom. So far, the structural deteminations for substituted butenes were already reported on the compounds [Carpenter & Park, 1987: (a)[1], Ahn & Carpenter, 1989: (b)[2]] and found that the skeletons of butenes were nearly planar.



(a) (b) (c)

It is also interesting to examine the stereochemistry and the consequences of the steric crowding.

EXPERIMENTAL

A colorless single crystal, 0.30×0.38×0.66 mm, was cut from a large block and mounted on a Nicolet R3m/E diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections ($25<2\theta<35°$). The $\theta-2\theta$ scan method at variable rates 4.9 to 29.3° min^{-1} and $2\theta_{max}=45°$ for the ranges $0\leq h\leq 13$, $0\leq k\leq 5$, $-17\leq l\leq 17$, was used. Three standard reflections monitored every 97 reflections showed with no decrease in intensity over the course of the data collection. Of 2241 measured intensities, 1877 unique data (not including space group absences) gave $R_{int}=0.017$, and 1762 data with $I>1.0\ \sigma(I)$ were used for refinement. Structure was solved by direct methods and all the H-atoms were found on a difference map; for refinement, all the C-H bond lengths were fixed at 0.96 Å and the methyl groups refined as rigid groups with ideal geometry; anisotropic thermal parameters were used for all the non-H atoms and fixed isotropic parameters for H-atoms (20% greater than that of carrying C-atoms). Refinement was carried out by cascade block-diagonal least-squares on F with the maximum $\sin\theta/\lambda=0.54$ $Å^{-1}$; the refinement of 172 parameters converged to $R=0.050$ and $wR=0.058$; $w=1/(\sigma^2(F)+0.0004\ F^2)$, where $\sigma^2(F)$ is from stati-

Table 1. Csrystal data

Chemical formula:	$C_{13}H_{17}NO_4S$
Molecular weight:	283.4
Csrystal system:	monoclinic
Space group:	$P2_1/c$
Unit cell parameters:	$a=13.194(7)$Å
	$b=7.290(4)$ $\beta=103.4(2)°$
	$c=16.532(14)$
	$Z=4$
	$V=1429.5$ Å^3
$\mu=2.2$ cm^{-1}	
$D_c=1.32$ g·cm^{-3}	
$F(000)=600$	
$\lambda=0.71069$ Å	
$T=298$ K	

Table 2. Fractional atomic coordinates ($\times10^4$) and thermal parameters (Å$^2\times10^3$) of Z-1-ethyl-2-nitro-1-butenyl-(4'-methyl)-phenyl sulfone. The e.s.d.'s are in parentheses

Atom	x	y	z	U^a
S	2199(1)	3544(1)	5502(1)	47(1)
O(1)	1220(2)	2481(3)	5542(1)	65(1)
O(2)	2864(2)	2985(3)	4940(1)	64(1)
O(3)	1669(3)	4894(4)	3462(1)	96(1)
O(4)	3245(3)	6252(4)	3928(2)	120(2)
N	2317(2)	5858(4)	3963(2)	70(1)
C(1)	3069(2)	3672(3)	6507(2)	41(1)
C(2)	4173(2)	4286(4)	6613(2)	46(1)
C(3)	4831(2)	4467(4)	7402(2)	51(1)
C(4)	4423(2)	4056(4)	8096(2)	50(1)
C(5)	3331(2)	3394(4)	7973(2)	50(1)
C(6)	2651(2)	3206(4)	7187(2)	47(1)
C(7)	5137(3)	4270(5)	8961(2)	76(1)
C(8)	1847(2)	6756(4)	4618(2)	47(1)
C(9)	1741(2)	5857(4)	5292(2)	43(1)
C(10)	1196(2)	6700(4)	5942(2)	54(1)
C(11)	1954(3)	7985(4)	6547(2)	66(1)
C(12)	1557(3)	8707(4)	4396(2)	66(1)
C(13)	877(3)	9054(5)	3531(2)	76(1)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalised U tensor. [b]Anisotropic thermal parameters of the non-H atoms and atomic coordinates of hydrogen atoms are available from the first author.

stics of counting; goodness of fit = 1.891. In the final cycle, it was found that $(\Delta/\sigma)_{max} = 0.23$ and the highest peak and the lowest in the final difference map, 0.33 and $-0.27\ e\text{Å}^{-3}$. Atomic scattering factors were from International Tables for X-ray Crystallography[4] and all calculations were performed on a Data General Eclips S140 computer using the SHELXTL 5.1 program package[5] (Nicolet Instrument Company, 1984).

RESULTS AND DISCUSSION

The crystal data for Z-1-ethyl-2-nitro-1-butenyl-(4'-methyl)-phenyl sulfone are given in *Table* 1 and *Table* 2 for its non-H atomic coordinates and thermal parameters. Bond lengths, bond angles

Table 3. Bond lengths (Å) bond angles (°) and selected trosion angles (°). The e.s.d.'s are in parentheses

(a) Bond lengths			
S-O(1)	1.438(2)	S-O(2)	1.427(3)
S-C(1)	1.755(3)	S-C(9)	1.784(3)
O(3)-N	1.225(4)	O(4)-N	1.183(5)
N-C(8)	1.488(4)	C(1)-C(2)	1.391(4)
C(1)-C(6)	1.380(4)	C(2)-C(3)	1.370(4)
C(3)-C(4)	1.384(4)	C(4)-C(5)	1.387(4)
C(4)-C(7)	1.500(4)	C(5)-C(6)	1.376(4)
C(8)-C(9)	1.325(4)	C(8)-C(12)	1.490(4)
C(9)-C(10)	1.518(4)	C(10)-C(11)	1.517(4)
C(12)-C(13)	1.499(4)		
(b) Bond angles			
O(1)-S-O(2)	118.7(1)	O(1)-S-C(1)	108.1(1)
O(2)-S-C(1)	108.7(1)	O(1)-S-C(9)	107.0(1)
O(2)-S-C(9)	110.1(1)	C(1)-S-C(9)	103.1(1)
O(3)-N-O(4)	125.4(3)	O(3)-N-C(8)	116.6(3)
O(4)-N-C(8)	117.6(3)	S-C(1)-C(2)	119.4(2)
S-C(1)-C(6)	120.1(2)	C(2)-C(1)-C(6)	120.4(2)
C(1)-C(2)-C(3)	119.1(3)	C(2)-C(3)-C(4)	121.6(3)
C(3)-C(4)-C(5)	118.2(2)	C(3)-C(4)-C(7)	121.8(3)
C(5)-C(4)-C(7)	120.0(3)	C(4)-C(5)-C(6)	121.3(3)
C(1)-C(6)-C(5)	119.3(3)	N-C(8)-C(9)	121.5(2)
N-C(8)-C(12)	110.5(2)	C(9)-C(8)-C(12)	128.0(3)
S-C(9)-C(8)	122.9(2)	S-C(9)-C(10)	114.4(2)
C(8)-C(9)-C(10)	122.6(2)	C(9)-C(10)-C(11)	114.6(3)
C(8)-C(12)-C(13)	116.4(3)		
(c) Torsion angles			
O(1)-S-C(1)-C(2)	166.4(2)	O(1)-S-C(1)-C(6)	−15.0(3)
O(2)-S-C(1)-C(2)	36.4(2)	O(2)-S-C(1)-C(6)	−145.1(2)
C(9)-S-C(1)-C(2)	−80.4(2)	C(9)-S-C(1)-C(6)	98.1(2)
O(1)-S-C(9)-C(8)	−119.2(2)	O(1)-S-C(9)-C(10)	59.6(2)
O(2)-S-C(9)-C(8)	11.1(3)	O(2)-S-C(9)-C(10)	−170.1(2)
C(1)-S-C(9)-C(8)	127.0(2)	C(1)-S-C(9)-C(10)	−54.3(2)
O(3)-N-C(8)-C(9)	80.7(3)	O(3)-S-C(8)-C(12)	−100.0(3)
O(4)-N-C(8)-C(9)	−105.4(3)	O(4)-S-C(8)-C(12)	73.9(3)
N-C(8)-C(9)-S	2.7(4)	N-C(8)-C(9)-C(10)	−175.9(2)
C(12)-C(8)-C(9)-S	−176.5(2)	C(12)-C(8)-C(9)-C(10)	4.9(4)
S-C(9)-C(10)-C(11)	101.7(2)	C(8)-C(9)-C(10)-C(11)	−79.5(3)

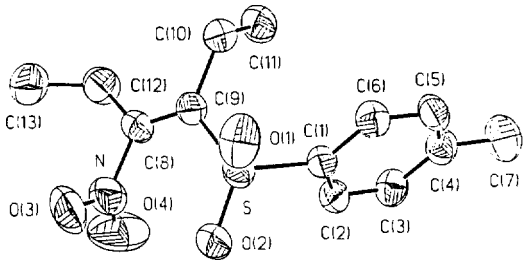


Fig. 1. The molecule of Z-1-ethyl-2-nitro-1-butenyl-(4'-methyl)-phenyl sulfone showing the atomic numbering scheme and thermal ellipsoid.

and selected torsion angles are given in *Table* 3. *Fig.* 1 is a thermal ellipsoid plot of the molecule showing the atomic numbering scheme. The substituted butene backbone of the molecule is nearly planar[3]: the mean plane of its six atoms C(8), C(9), C(10), C(12), N and S is given by the equation $9.960x + 2.258y + 4.696z = 5.536$, where x, y and z are in Å, and the maximum deviation from this plane is 0.045 Å for the N atom. The metylbenzene portion is also nearly planar: the mean plane of its seven atoms C(1) through C(7) is $-4.180x + 6.844y + 1.828z = 2.402$ and the maximum deviation from this plane is 0.018 Å for the C(1) atom.

The angle between these planes is 88.5°. The nitro group O(3)-N-O(4) makes an angle of 78.6° with the butene backbone. The angle of this nitro butene portion differs significantly from the angles of the previously reported structure: 8.9° in *cis*-3-nitro-2-thiocyanato-2-butene[1] (Carpenter & Park, 1987) and 4.3~9.4° in Z-3-p-tolythio-4-nitro-3-hexene[2](Ahn & Carpenter, 1987). The methyl carbon C(11) is 1.287 Å above the plane of the butene backbone and C(13) is 0.961 Å below. No short intermolecular contacts appear. The nitro group in the present structure is twisted almost 69~74° further out of the plane of the butene backbone, as compared with the data reported. The C(8)-N bond is 0.045 Å longer than that of 1.443(3)Å in *cis*-3-nitro-2-thiocyanato-2-butene, and the C(8)-C (9) double bond is 0.027 Å shorter than that of 1.352(3)Å. The similar elongation and shortening are also found in Z-3-p-tolythio-4-nitro-3-hexene. All these differences correspond to much reduced contribution of resonance structure involving the nitro group. Rotation of the nitro group out of the butene plane appears to be the result of repulsion between O(2) and O(3), 2.894 Å apart (expected van der Waals distance 2.80 Å).

ACKNOWLEDGEMENT

The first author thanks the Department of Chemistry, Brown University for alowing him to use a Nicolet R3m/E diffractometer system for data collecton and refinement. We acknowledge the assistance of Dr. Paul G. Williard in data collection.

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