DAEHAN HWAHAK HWOEJEE
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Z-3 - 파라 - 톨릴치오 -4 - 니트로 -3 - 헥센의 결정 및 분자구조

安重泰† · Gene B. Carpenter *
한국외국어대학교 자연과학대학 화학과
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The Crystal and Molecular Structure of Z-3-P-Tolylthio-4-Nitro-3-Hexene

Choong Tai Ahn† and Gene B. Carpenter*
Department of Chemistry, College of Natural Sciences, Hankuk University of Foreign Studies, Seoul 130-791, Korea
**Department of Chemistry, Broun University, Providence, Rhode Island 02912, U. S. A.*
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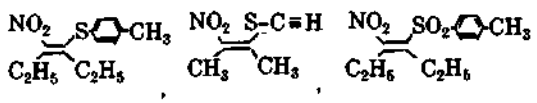
요 약. Z-3-파라-톨릴치오-4-니트로-3-헥센의 결정은 단사정계에 속하며 $a=13.756(3)$, $b=9.310(4)$, $c=21.305(3)$ Å, $\beta=95.0°$이며 단위세포안에 8개의 분자가 있으며 $2.0\sigma(I)$ 보다 큰 강도를 가진 2935개의 회절반점에 대하여 계단식 대각 최소자승법에 의하여 정밀화된 최종 R값은 0.085이다. 직접법에 의하여 구조를 풀었으며 C-H 결합길이와 메칠기는 길이를 고정시켜 이상적인 기하학적구조에 맞도록 하여 계산을 정밀화하였다. 두 분자 A와 B는 끝의 두 에칠기를 제외하고는 거의 유사한 구조를 갖고 있다. 니트로기를 포함한 에틸렌 모양의 골격은 메칠벤젠기에 대하여 거의 수직으로 되어 있으며 두 에틸기는 시스-형 구조를 가지고 있으나 끝부분의 메칠기는 A분자에서는 그의 골격에 대해 서로 반대방향으로 향하고 있고 B분자는 같은 방향으로 향하고 있다. 결정내 분자들은 비결합성 van der Waals 힘으로 쌓여져 있다.

ABSTRACT. The title compound ($C_{13}H_{17}NO_2S$) is monoclinic, space group $P2_1/a$, with $a=13.756(3)$, $b=9.310(4)$, $c=21.305(3)$ Å, $\beta=95.0°$, $Z=8$, $V=2718.11$ Å^3, $D_c=1.23$ g.cm^{-3}, (Mo Kα)$=0.71069$ Å, $\mu=2.18$ cm^{-1}, $F(000)=1071.86$, $T=298$, $R=0.085$ for 2935 unique observed reflections with $I \geqslant 2.0\sigma(I)$. The structure was solved by direct methods. The C-H bond lengths and the methyl groups are fixed and refined as their ideal geometry by allowing to ride on the parent atoms. Both molecules A and B have almost same structures except for two terminal ethyl groups. The ethylene-like skeleton including the nitro group in one molecule is nearly perpendicular to the plane of the methylbenzene group and two ethyl groups form a *cis*-type structure which has the different orientations between two molecules; in the molecule A, two terminal methyl groups being the opposite directional arrangement against the plane of its skeleton, while in the B, with the same directional structure from its plane. The molecules in the crystal are packed together by non-bonded van der Waals forces.

INTRODUCTION

Z-3-p-tolylthio-4-nitro-3-hexene (1) is one of a series of multiply substituted butenes;



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The structural determinations of *cis*-3-nitro-2-thiocyanato-2-butene(11)[1] and Z-1-ethyl-2-nitro-1-butenyl-(4'-methyl)-phenyl-sulfone (111)[2] were already reported. To confirm the stereochemistry and to examine the consequences of their conformations and the steric crowdings, the structure analysis of the title compound was undertaken to continue as part of studies.

EXPERIMENTAL

The title compounds were kindly synthesized and supplied by Dr. K.P. Park, KAIST, Dong Dae Mun, Seoul, Korea. Pale-yellow single crystals, 0.5×0.4×0.6 mm, were cut from a large block. The crystal was fixed using paste for the data collection because epoxy cement caused decomposition of the crystal.

Accurate lattice parameters from 25 reflections in 2θ ranges 25-35° were measured with graphite monochromatized Mo K α radiation ($\lambda = 0.71069$ Å) on the Nicolet R3m/E diffractometer. The intensities were recorded by θ-2 θ scan technique at variable rates 4.9-29.3°/min. with $2\theta_{max} = 45°$ for the ranges $-13 \leq h \leq 13$, $0 \leq k \leq 9$, $0 \leq l \leq 21$. Three standard reflections monitored every 97 reflections showed no signicant variation in intensity throughout data collection. Lorentz and polarization factors were applied. No corrections were made for absorption or secondary extinction.

Table 1. Crystal data

Chemical formula: $C_{13}H_{17}NO_2S$	
Molecular weight: 251.37	
Crystal system: monoclinic	
Space group: $P2_1/a$	
Unit cell parameters:	$a = 13.756(3)$Å)
	$b = 9.310(4)$ $\beta = 95.0°$
	$c = 21.305(3)$
	$V = 2718.11$ Å^3
	$Z = 8$
μ(Mo Kα): 2.18 cm^{-1}	
D_c: 1.23 g·cm^{-3}	
F(000): 1071.86	

3443 independent reflections were measured, giving 2935 observed ($I > 2.0\sigma(I)$) reflections used in the refinement with $R_{int} = 0.022$. The structure was solved by direct methods using 200 reflections of which E values greater than 1.56. The E map revealed positions of all non- hydrogen atoms. All the hydrogen atoms were included at calculated positions with C-H = 0.96 Å though a difference Fourier synthesis revealed the positions of several hydrogen atoms. The hydrogen atoms were assigned to the isotropic temperature factors $u_{eq} = 0.076$ Å^2 and allowed to ride on their parent atoms. The methyl groups were refined as rigid groups with ideal geometry. All the non-hydrogen atoms were refined anisotropically. The refinement was carried out by cascade block-diagonal least sequares on F with the maximum $(\sin\theta)/\lambda = 0.54$ Å^{-1} and with 298 least squares parameters. The final refinement was converged at R = 0.085 and wR = 0.099, where $w = 1/(\sigma^2(F) + 0.0003\ F^2)$; $\sigma^2(F)$ from statistics counting, goodness of fit = 3.674. The maximum shift/e.s.d. was 0.075 and the final difference Fourier map showed the peaks; the maximum difference peak 0.925 eÅ^{-3} and the minimum difference peak -0.711 eÅ^{-3}

The atomic scattering factors were taken from International Tables for X-ray Crytallography (1974)[3] and all calculations were performed on a Data General Eclips S140 computer using the SHELXTL 5.1 program package (Nicolet Instrument Company, 1984).[4]

The crystal data are listed in *Table* 1.

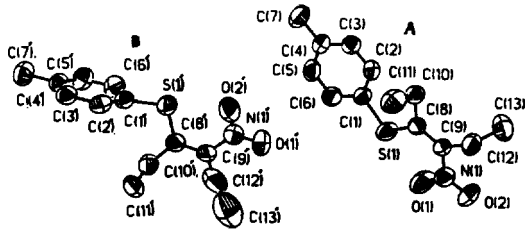

Fig. 1. Molecules of-Z-3-*p*-tolylthio-4-nitro-3-hexene showing the atomic numbering scheme and thermal ellipsoids.

Table 2. Fractional atomic coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for Z-3-*p*-tolylthio-4-nitro 3-hexene. The e.s.d.'s are in parentheses.

Atom	*x*	*y*	*z*	*u**
S(1)	47(1)	9632(2)	8666(1)	76(1)
S(1')	468(1)	7583(2)	4455(1)	82(1)
O(1)	-1205(3)	11093(5)	9222(2)	109(2)
O(2)	-1002(3)	12955(5)	9801(2)	98(2)
O(1')	-517(3)	8666(5)	6228(2)	114(2)
O(2')	554(3)	8474(6)	5589(2)	116(2)
N(1)	-6883)	12064(5)	9456(2)	75(2)
N(1')	-282(4)	8448(5)	5692(2)	77(2)
C(1)	919(3)	8566(5)	8298(2)	57(2)
C(2)	1480(4)	7568(5)	8648(3)	66(2)
C(3)	2078(4)	6639(5)	8351(2)	64(2)
C(4)	2117(4)	6675(6)	7708(2)	63(2)
C(5)	1535(4)	7669(6)	7370(3)	74(2)
C(6)	940(4)	8605(5)	7653(2)	69(2)
C(7)	2747(4)	5646(7)	7383(3)	96(3)
C(8)	701(3)	11122(5)	8968(2)	54(2)
C(9)	326(3)	12156(5)	9305(2)	57(2)
C(10)	1759(3)	11269(5)	8818(2)	64(2)
C(11)	1829(4)	12113(6)	8207(3)	89(3)
C(12)	847(4)	13447(5)	9585(2)	73(2)
C(13)	1276(5)	13253(7)	10253(3)	106(3)
C(1')	437(3)	6804(5)	3691(2)	60(2)
C(2')	570(3)	7630(5)	3177(3)	66(2)
C(3')	679(3)	6987(6)	2593(3)	68(2)
C(4')	650(3)	5524(5)	2519(2)	62(2)
C(5')	525(4)	4711(6)	3039(3)	78(2)
C(6')	431(4)	5317(7)	3619(3)	81(2)
C(7')	763(4)	4858(7)	1895(3)	90(2)
C(8')	-739(3)	7699(5)	4609(2)	65(2)
C(9')	-1002(3)	8053(6)	5190(2)	84(2)
C(10')	-1522)3)	7425(6)	4090(2)	78(2)
C(11')	-1759(3)	8729(6)	3677(2)	95(3)
C(12')	-2018(3)	7872(6)	5395(2)	167(5)
C(13')	-2518(3)	9297(6)	5492(2)	184(6)

*Equivalent isotropic u defined as one third of the trace of the orthogonalized u tensor.

Table 3. Hydrogen coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for Z-3-*p*-tolylthio-4-nitro -3-hexene.

Atom	*x*	*y*	*z*	*u**
H(2)	1459	7523	9096	72
H(3)	2467	5954	8599	79
H(5)	1545	7701	6920	89
H(6)	548	9287	7406	83
H(7a)	2684	5833	6938	112
H(7b)	2544	4679	7458	112
H(7c)	3415	5767	7544	112
H(10a)	2119	11765	9158	78
H(10b)	2034	10332	8771	78
H(11a)	2501	12198	8122	102
H(11b)	1558	13054	8252	102
H(11c)	1472	11621	7864	102
H(12a)	1368	13678	9331	86
H(12b)	394	14233	9576	86
H(13a)	1598	14118	10402	120
H(13b)	1738	12479	10269	120
H(13c)	763	13028	10515	120
H(2')	593	8657	3217	73
H(3')	772	7585	2236	77
H(5')	507	3684	3000	97
H(6')	353	4717	3977	95
H(7'a)	839	5592	1586	104
H(7'b)	195	4294	1769	104
H(7'c)	1329	4250	1927	104
H(10'a)	-1293	6670	3833	91
H(10'b)	-2107	7118	4266	91
H(11'a)	-2247	8478	3345	104
H(11'b)	-1180	9046	3497	104
H(11'c)	-2000	9487	3927	104
H(12'a)	-2402	7340	5077	183
H(12'b)	-1977	7347	5784	183
H(13'a)	-3159	9126	5622	211
H(13'b)	-2568	9830	5105	211
H(13'c)	-2143	9837	5812	211

121.75(5) C(8) a.

RESULTS AND DISCUSSION

Fig. 1. depicts a thermal-ellipsoid plot for a pair of molecules A and B showing the atomic numbering scheme in an asymmetric unit. Final fractional atomic coordinates and their equivalent isotropic temperature factors for non-hydrogen and hydrogen atoms are listed in *Table* 2 and 3.

Table 4 and 5 give bond lengths and bond angles for two molecules. Compared with both molecules, as can be seen in Tables, there are slight differences between bond lengths and bond angles with the maximum values 0.029 Å in C(8)- C(9) and with the maximum 2.7° in C(8)-C(9)- C(12). The average bond length and bond angle for the

Table 4. Bond lengths(Å) for Z-3-p-tolythio-4-nitro-3-hexene. The e.s.d.'s are in parentheses

Molecule A		Molecule B	
S(1)–C(1)	1.789(5)	S(1')–C(1')	1.778(5)
S(1)–C(8)	1.745(5)	S(1')–C(8')	1.723(5)
O(1)–N(1)	1.228(7)	O(1')–N(1')	1.229(6)
O(2)–N(1)	1.212(6)	O(2')–N(1')	1.190(7)
N(1)–C(9)	1.461(6)	N(1')–C(9')	1.442(6)
C(1)–C(2)	1.384(7)	C(1')–C(2')	1.364(7)
C(2)–C(3)	1.382(7)	C(2')–C(3')	1.402(8)
C(3)–C(4)	1.377(7)	C(3')–C(4')	1.371(7)
C(4)–C(5)	1.384(7)	C(4')–C(5')	1.364(7)
C(5)–C(6)	1.371(8)	C(5')–C(6')	1.374(8)
C(6)–C(1)	1.378(7)	C(6')–C(1')	1.393(8)
C(4)–C(7)	1.501(8)	C(4')–C(7')	1.488(8)
C(8)–C(10)	1.523(6)	C(8')–C(10')	1.498(6)
C(10)–C(11)	1.531(8)	C(10')–C(11')	1.518(7)
C(9)–C(12)	1.497(7)	C(9')–C(12')	1.508(6)
C(12)–C(13)	1.504(8)	C(12')–C(13')	1.517(7)
C(8)–C(9)	1.331(7)	C(8')–C(9')	1.360(6)

Table 5. Bond angles(o) for Z-3-p-tolythio-4-nitro-3-hexene. The e.s.d.'s are in parentheses

Molecule A		Molecule B	
C(1)–S(1)–C(8)	105.0(2)	C(1')–S(1')–C(8')	104.6(2)
O(1)–N(1)–O(2)	121.7(5)	O(1')–N(1')–O(2')	120.3(5)
O(2)–N(1)–C(9)	119.4(4)	O(2')–N(1')–C(9')	118.8(4)
O(1)–N(1)–C(9)	118.9(5)	O(1')–N(1')–C(9')	120.8(5)
S(1)–C(1)–C(2)	120.1(4)	S(1')–C(1')–C(2')	120.7(4)
S(1)–C(1)–C(6)	119.7(4)	S(1')–C(1')–C(6')	120.5(4)
C(2)–C(1)–C(6)	119.7(5)	C(2')–C(1')–C(6')	118.1(5)
C(1)–C(2)–C(3)	120.0(5)	C(1')–C(2')–C(3')	120.3(5)
C(2)–C(3)–C(4)	121.0(5)	C(2')–C(3')–C(4')	121.4(5)
C(3)–C(4)–C(5)	117.6(5)	C(3')–C(4')–C(5')	117.6(5)
C(4)–C(5)–C(6)	122.5(5)	C(4')–C(5')–C(6')	122.0(5)
C(5)–C(6)–C(1)	119.1(5)	C(5')–C(6')–C(1')	120.5(5)
C(3)–C(4)–C(7)	121.2(5)	C(3')–C(4')–C(7')	120.7(5)
C(5)–C(4)–C(7)	121.2(5)	C(5')–C(4')–C(7')	121.7(5)
S(1)–C(8)–C(9)	124.2(4)	S(1')–C(8')–C(9')	121.7(3)
S(1)–C(8)–C(10)	117.7(3)	S(1')–C(8')–C(10')	119.4(4)
C(9)–C(8)–C(10)	118.0(4)	C(9')–C(8')–C(10')	118.8(4)
C(8)–C(10)–C(11)	110.9(4)	C(8')–C(10')–C(11')	113.3(3)
C(8)–C(9)–N(1)	119.9(4)	C(8')–C(9')–N(1')	121.1(4)
C(8)–C(9)–C(12)	126.9(4)	C(8')–C(9')–C(12')	124.2(2)
N(1)–C(9)–C(12)	113.1(4)	N(1')–C(9')–C(12')	114.1(2)
C(9)–C(12)–C(13)	114.6(5)	C(9')–C(12')–C(13')	112.6(3)

benzene rings are 1.379(7) Å in the molecules A and 1.378(7) Å in the B with the same bond angles as 119.9(5)° in both molecules. The benzene rings are coplanar with the maximum deviation of −0.008 Å in the C(2) of the molecule A and with that of −0.013 Å in the C(6) of the B.

The C–S lengths connecting between the benzene ring and 4-nitro-3-hexene group, both 1.789(5) Å and 1.778(5) Å, are slightly longer than those observed in *p*-methylbenzenesulfonate derivatives (1.760(4) Å and 1.781(8) Å).[5] The C(8)–S(1) and the C(8')–S(1') lengths between the hexene groups and the sulfur atoms are 1.745(8) Å and 1.723(5) Å, which are a little shorter than those reported in *cis*-3-nitro-2-thiocyanato-2-butene (1.772(2) Å).[1] The C(8)–C(9) length of 1.331(7) Å and the C(8')–C(9') length of 1.360(6) Å which have double bond character in the molecules form the skeletons of the ethylene-like shape with the angles S(1)–C(8)– C(10) = 117.3 (3)°, S(1')–C(8')–C(10') = 119.4(4)°, N(1)–C(9)– C(12) = 113.1(4)°, and N(1')–C(9')– C(12') = 114.1 (2)°, respectively. The maximum deviations from the least-square planes of their ethylene-like skeletons are −0.014 Å of C(12) in the molecule Å and 0.176 Å of C(12') in the B. In hexene groups of both molecules, each two ethyl groups of the molecule form a *cis*-type structure. On the other hand, one terminal C(11)-methyl group of the molecule Å is deviated by 1.445 Å upwards from its least-squares plane, while the other C(13)-methyl group by 1.387 Å downwards. In the molecule B, however, both terminal C(11')- and C(13')- methyl groups are deviated downwards by −1.505 Å and −1.073 Å from its plane respectively. The C–C bond lengths of four ethyl groups range from 1.497 Å to 1.531 Å, and the bond angles from 110.9° to 114.6°.

Each nitro group including the carbon atom attached is nearly coplanar from its least-squares plane with the deviation of −0.005 Å in the N(1) of the molecule A, and that of 0.023 Å in the N(1')

Table 6. Selected torsion angles(o) for Z-3-p-tolythio-4-nitro-3-hexene. The e.s.d.'s are in parentheses

Molecule A		Molecule B	
C(8)-S(1)-C(1)-C(2)	87.2(4)	C(8')-S(1')-C(1')-C(2')	103.1(4)
C(8)-S(1)-C(1)-C(6)	-101.3(4)	C(8')-S(1')-C(1')-C(6')	-87.2(4)
C(1)-S(1)-C(8)-C(9)	-176.8(4)	C(1')-S(1')-C(8')-C(9')	170.3(4)
C(1)-S(1)-C(8)-C(10)	5.2(4)	C(1')-S(1')-C(8')-C(10')	-10.6(5)
S(1)-C(8)-C(10)-C(11)	89.8(5)	S(1')-C(8')-C(10')-C(11')	-83.3(4)
S(1)-C(8)-C(9)-N(1)	1.6(7)	S(1')-C(8')-C(9')-N(1')	4.5(7)
S(1)-C(8)-C(9)-C(12)	179.1(4)	S(1')-C(8')-C(9')-C(12')	-166.5(2)
C(10)-C(8)-C(9)-N(1)	179.6(4)	C(10')-C(8')-C(9')-N(1')	-174.6(3)
C(10)-C(8)-C(9)-C(12)	-2.9(7)	C(10')-C(8')-C(9')-C(12')	14.4(7)
C(8)-C(9)-C(12)-C(13)	-92.8(6)	C(8')-C(9')-C(12')-C(13')	-111.5(4)
O(1)-N(1)-C(9)-C(8)	-6.3(7)	O(1')-N(1')-C(9')-C(8')	-174.7(5)
O(2)-N(1)-C(9)-C(8)	174.7(5)	O(2')-N(1')-C(9')-C(8')	0.8(8)
O(2)-N(1)-C(9)-C(12)	-3.1(7)	O(2')-N(1')-C(9')-C(12')	-2.9(6)
O(1)-N(1)-C(9)-C(12)	175.9(5)	O(1')-N(1')-C(9')-C(12')	172.6(4)
C(9)-C(8)-C(10)-C(11)	-88.3(5)	C(9')-C(8')-C(10')-C(11')	95.9(5)
C(2)-C(3)-C(4)-C(7)	-178.5(5)	C(2')-C(3')-C(4')-C(7')	179.8(4)
C(7)-C(4)-C(5)-C(6)	178.8(5)	C(7')-C(4')-C(5')-C(6')	179.2(5)

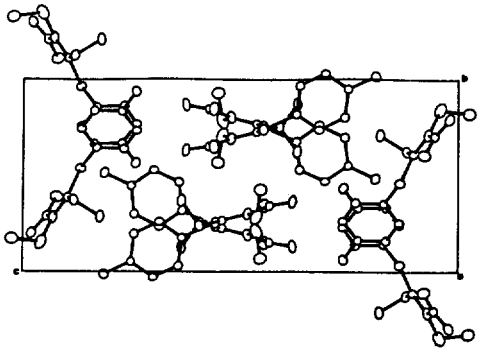

Fig. 2a. The crystal structure of Z-3*p*-tolylthio-4 nitro 3 hexene in projection down the a-axis. Atoms are shown as 10% probability elliposoids.

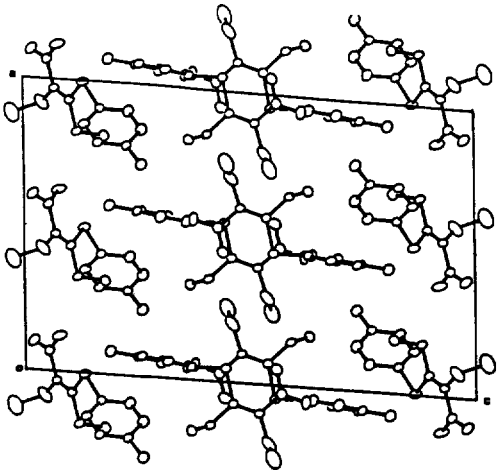

Fig. 2b. The crystal structure of Z-3-*p*-tolylthio 4-nitro-3-hexene in projection down the b-axis. Atoms are shown as 15% probability ellipsoids.

of the B, which have the sp^2 type angles O(1)-N(1)-O(2)=121.7(5)° and O(1')-N(1')-O(2')=120.3 (5)°, respectively. The N-O bond lengths of the nitro groups range from 1.190 Å to 1.229 Å.

The methyl benzene groups including the sulfur atoms are tilted by 95.3° and 96.7° from the planes of their ethylene-like skeletons respectively. The NO_2 group including a carbon atom is almost perpendicular to the plane of the methylbenzene group with the angles 81.4° in the molecule A and 79.9° in the B respectively. The plane of the sulfur containing triangle (C(1)-S(1)- C(8)) is also nearly perpendicular to the plane of the methylbenzene group with the angles, 96.9° in the molecule A and 97.8° in the B. As the result, the nitro group is tilted by 4.3° in the A and by 9.4° in the B from the plane of its ethylene-like skeleton. *Table* 6. gives the selected torsion angles for molecules A and B.

Fig. 2a and 2b give the projections of the structures along the axes. The molecules are packed together by non-bonded van der Waals forces.

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