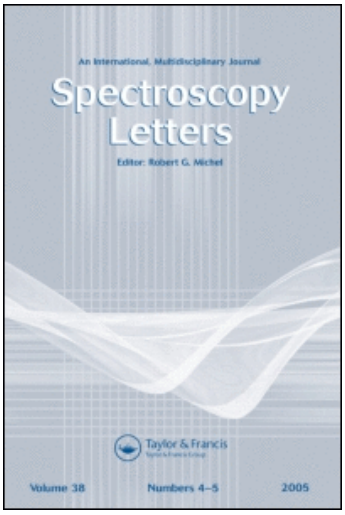


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Structure of 4,4'-butane-(1,4,7-three-p-tolylsulphonyl-1,4,7-three amine) diphthalonitrile

Sema Özturk[a]; Şamil Işik[b]; Erbil Aguar[c]; Selami Şalsmaz[d]; H. K. Fun[e]; Ahmet Erdönmez[b]
[a] Department of Physics, Erciyes University, Kayseri, Turkey [b] Department of Physics, Ondokuz Mayis University, Samsun, Turkey [c] Department of Chemistry, Ondokuz Mayis University, Samsun, Turkey [d] Department of Chemistry, KTU, Art and Science Faculty, Rize, Turkey [e] School of Physics, X-ray Crystallography Unit, Univ. Sains Malaysia, Penang, Malaysia

To cite this Article Özturk, Sema , Işik, Şamil , Aguar, Erbil , Şalsmaz, Selami , Fun, H. K. and Erdönmez, Ahmet(2000) 'Structure of 4,4'-butane-(1,4,7-three-p-tolylsulphonyl-1,4,7-three amine) diphthalonitrile', Spectroscopy Letters, 33: 2, 245 — 254
To link to this Article: DOI: 10.1080/00387010009350074
URL: http://dx.doi.org/10.1080/00387010009350074

SPECTROSCOPY LETTERS, 33(2), 245–254 (2000)

Structure of 4,4'-butane-(1,4,7-three-p-tolylsulphonyl-1,4,7-three amine) diphthalonitrile

Key Words: Crystal Structure, Phthalocyanines

Sema ÖZTURK[a], Şamil IŞIK*[b], Erbil AĞAR[c], Selami ŞAŞMAZ[d], H. K. FUN[e], Ahmet ERDÖNMEZ[b]

a Erciyes University, Department of Physics, TR-38039 Kayseri-Turkey

b Ondokuz Mayıs University, Department of Physics, TR-55139 Samsun –Turkey

c Ondokuz Mayıs University, Department of Chemistry, TR-55139 Samsun –Turkey

d KTU, Art and Science Faculty, Department of Chemistry, Rize –Turkey

e X-ray Crystallography Unit, Univ. Sains Malaysia, School of Physics, Penang Malaysia

Abstract

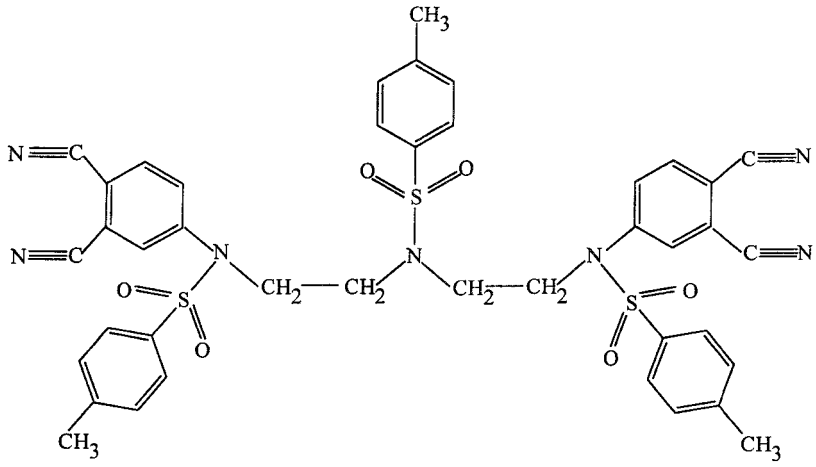
The crystal structure of the title compound, $C_{41}H_{35}N_7O_6S_3$ was determined as monoclinic by single crystal X-Ray diffraction technique.The molecular structure was identified by IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis. The crystal parameters of this compound are as follows: monoclinic P 2 1/n, a = 12.694(2) Å, b = 26.204(2) Å, c = 13.005(2) Å, β = 102.95(2)°, V = 4216.02(1) Å^3, Z = 4, Dx = 1.289 g/cm^3, F(000) = 1704, λ (MoKα) = 0.71070 Å, μ = 0.2 mm^{-1}. The structure was solved by SHELXS-97 and refined by SHELXL-97. R = 0.06 for 3178 observed reflections with I > 2σ (I).

* Correspondence author: Dr. Şamil IŞIK, Department of Physics, Faculty of Art and Sciences, Ondokuz Mayıs University, Kurupelit TR-55139 – SAMSUN / TURKEY. e-mail=samili@samsun.omu.edu.tr ; Fax: 00 90 362 4576081

Introduction

Unsubstitued and substituted phthalocyanines are widely used as pigments and dyes[1]. Owing to their thermal stability and facile accessibility, metallophthalocyanines have been of great interest in the preparation of organic conductors and semiconductors. Using different main group or transition metals in the center of the macrocycles, oxygen-bridged, e.g. [Pc(SiO)]n (Pc:phthalocyanine) and other bridged systems with organic ligands, e.g. [Pc(FeL)]n with L: e.g. pyrazine, disocyanobenzene and tetrazine, can be obtained, exhibiting good semiconducting properties with and without doping. One of the important aims of research in the chemistry of phthalocyanines is to enhance their solubility in various solvents.

As part of the investigations of the synthesis of polymeric phthalocyanines, (I), title compound was obtained and its structure was analyzed by standard analytical techniques (microanalysis, NMR, IR). In order to obtain information about the stereochemistry of the molecule and to confirm the assigned structure, the x-ray analysis of (I) was undertaken.



(I)

Experimental

Butane-1,4,7-three-p-tolylsulphonyl-1,4,7-threeamine (16.95 g., 30 mmol) was dissolved in dry DMF (200 ml) under nitrogen and 4-nitrophthalonitrile (10.38 g., 60 mmol)

was added. After stirring for 10 min. finely ground anhydrous K2CO3 (20.7 g., 150 mmol) was added portion wise in 2h. with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 20 h. Water (500 ml) was then added and the product filtered and washed with water until the filtrate was neutral. The product was then refluxed in methanol, filtered and the residue washed with hot methanol and diethyl ether and dried. The compound was recrystallized as single crystals in chloroform.

4,4'-butane-(1,4,7-three-p-tolylsulphonyl-1,4,7-three amine) diphthalonitrile

Yield: 20 g. (81.6 %), m.p.: 210-211 °C.

IR(KBr): 3080-2880 (CH), 2220 (CN), 1590, 1495, 1450, 1345 (SO_2), 1160 (SO_2), 1090, 1060, 1015-1000, 950, 810, 750-730, 695 cm^{-1}

^{1}H-NMR ($CDCL_3$) δ: 7.81-7.26 (m, Ar, 18H), 3.93-3.86 (t, CH_2, 4H), 3.28-3.20 (t, CH_2, 4H), 2.45 (s, CH_3, 9H) ppm.

^{13}C-NMR ($CDCL_3$) δ: 145.34, 144.02, 134.46, 133.12, 132.02, 131.79, 130.28, 127.41, 126.89, 116.69, 114.84, 113.92, 49.28, 48.56, 21.49 ppm.

x-ray diffraction:

A summary of the key crystallographic information is given in Table - 1. Data collection was carried out using a Siemens SMART[2] CCD diffractometer at 298 K. Preliminary cell constants were obtained from 30 narrow frames (frame width = 0.3° in ω) data. Final cell parameters were obtained by global refinement of reflections obtained from integration of all the frame data. A total of 7437 frames of intensity data were collected with a frame width of 0.3° in ω and a counting time of 30 s per frame at a crystal-to-detector distance of 3 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using the preliminary cell orientation matrix. The integration process yielded a total of 25428 reflections (less than fivefold redundancy), of which 7344 were independent reflections ($2\theta_{max}$ = 50°). The first 50 frames of data were collected at the end of data collection to monitor crystal decay. No crystal decay was observed for this data set. The collected data were reduced by using the program SAINT [2] and emprical absorption correction was carried out by using the SADABS [3] program.

The structure was solved by direct methods using SHELXS - 97[4] and refined by full matrix least squares using SHELXL – 97[5]. All atoms except H were refined anisotropically. H-atoms were located geometrically and then refined isotropically with fixed displacement parameters. The final conventional R(F) = 0.067 and wR(F^2) = 0.1227 for

Table 1.

Summary of crystal data and structure refinement for $C_{41}\ H_{35}\ N_7\ O_6\ S_3$

Formula	$C_{41}\ H_{35}\ N_7\ O_6\ S_3$
Formula Weight	817.97
Color	light yellow
Crystal System	Monoclinic
Space group(no.) ; Z	P21/n (No. 14) ; 4
Lattice constants (T = 293 K)	a=12.6944(3)Å; b=26.2046(3)Å; c=13.0047(2)Å; β = 102.949(1)°
Volume V [$Å^3$]	4216.02(1)
D_x [$g.cm^{-3}$]	1.289
F (000)	1704
μ [mm^{-1}]	0.23
Radiation [Å]	MoKα (= 0.71073 Å)
Crystal Size [mm]	0.42 x 0.14 x 0.08
θ range [°]	1.55 to 25.00
h, k, l	-15/12, -31/31, -10/15
reflection collected / unique	25428 / 7344
R_{int}	0.09
Independent reflection	3178
Absorption correction	Emprical using SADABS
No. Parameters	517
Final R indices [I≥2σ(I)]	R = 0.067, wR = 0.1220
Min and Max resd. Density	-0.349, 0.353[e / $Å^3$]

Table 2.

Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for C_{41} H_{35} N_7 O_6 S_3. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

$$U_{eq} = \left(\frac{1}{3}\right)\sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

Atom	x	y	z	U(eq)
S1	0.2125(1)	0.3924(4)	0.1568(8)	0.065(5)
S2	0.3292(1)	0.2117(4)	0.3713(9)	0.065(5)
S3	0.3540(2)	0.3557(6)	0.6825(1)	0.107(7)
O1	0.1864(3)	0.4076(1)	0.2543(2)	0.076(1)
O2	0.3131(3)	0.4072(1)	0.1333(2)	0.082(1)
O3	0.3467(3)	0.1913(1)	0.2750(2)	0.086(1)
O4	0.4190(2)	0.2295(1)	0.4504(2)	0.087(1)
O5	0.4397(4)	0.3212(2)	0.6796(3)	0.169(2)
O6	0.3003(4)	0.3559(1)	0.7688(3)	0.132(2)
N1	0.2101(3)	0.3292(2)	0.1556(2)	0.058(1)
N2	0.2476(3)	0.2608(1)	0.3394(2)	0.053(1)
N3	0.2604(4)	0.3439(1)	0.5750(3)	0.081(1)
N4	0.1071(4)	0.2110(2)	-0.2400(4)	0.124(2)
N5	0.4214(4)	0.1926(2)	-0.1914(3)	0.103(2)
N6	-0.0815(5)	0.4772(3)	0.3364(5)	0.158(3)
N7	-0.2614(6)	0.4108(4)	0.5212(6)	0.236(5)
C1	-0.0546(5)	0.4435(2)	-0.1145(4)	0.086(2)
C2	-0.0739(4)	0.4394(2)	-0.0141(4)	0.078(2)
C3	0.0082(4)	0.4238(2)	0.0694(4)	0.073(2)
C4	0.1088(4)	0.4122(1)	0.0529(3)	0.059(2)
C5	0.1282(5)	0.4167(2)	-0.0474(4)	0.085(2)
C6	0.0461(6)	0.4320(2)	-0.1295(4)	0.095(3)
C7	-0.1452(5)	0.4605(2)	-0.2063(4)	0.119(3)
C8	0.2537(3)	0.3036(2)	0.0777(3)	0.054(2)
C9	0.1863(3)	0.2802(2)	-0.0076(3)	0.062(2)
C10	0.2308(3)	0.2531(2)	-0.0786(3)	0.059(2)
C11	0.3420(4)	0.2493(2)	-0.0648(3)	0.064(2)
C12	0.4093(3)	0.2736(2)	0.0196(3)	0.069(2)
C13	0.3644(3)	0.2997(2)	0.0910(3)	0.065(2)
C14	0.1615(4)	0.2288(2)	-0.1679(4)	0.082(2)
C15	0.3868(4)	0.2185(2)	-0.1366(4)	0.075(2)
C16	0.1214(3)	0.3041(2)	0.1926(3)	0.061(2)
C17	0.1579(3)	0.2540(1)	0.2458(3)	0.058(2)
C18	0.2582(4)	0.1672(2)	0.4295(3)	0.059(2)
C19	0.2728(4)	0.1647(2)	0.5378(3)	0.077(2)
C20	0.2085(6)	0.1317(2)	0.5816(4)	0.100(3)
C21	0.1292(5)	0.1025(2)	0.5197(5)	0.103(3)
C22	0.1173(5)	0.1048(2)	0.4122(5)	0.103(3)
C23	0.1803(4)	0.1370(2)	0.3670(3)	0.078(2)
C24	0.0586(6)	0.0668(3)	0.5673(5)	0.173(4)
C25	0.2172(3)	0.2852(2)	0.4303(3)	0.062(2)
C26	0.2913(3)	0.3288(2)	0.4772(3)	0.067(2)

continued

Table 2. Continued

C27	0.1530(4)	0.3622(2)	0.5667(3)	0.066(2)
C28	0.1086(4)	0.3979(2)	0.4906(3)	0.063(2)
C29	0.0027(4)	0.4124(2)	0.4777(3)	0.071(2)
C30	-0.0609(5)	0.3919(2)	0.5417(4)	0.090(3)
C31	-0.0158(6)	0.3574(2)	0.6183(4)	0.103(3)
C32	0.0885(6)	0.3425(2)	0.6307(3)	0.091(3)
C33	-0.0430(5)	0.4487(2)	0.3985(5)	0.104(3)
C34	-0.1733(7)	0.4029(3)	0.5294(5)	0.149(4)
C35	0.4008(5)	0.4173(2)	0.6686(3)	0.086(2)
C36	0.5004(6)	0.4260(3)	0.6387(4)	0.122(3)
C37	0.5322(6)	0.4762(5)	0.6322(5)	0.133(3)
C38	0.4739(7)	0.5159(4)	0.6497(5)	0.125(3)
C39	0.3772(6)	0.5064(3)	0.6769(4)	0.109(3)
C40	0.3403(5)	0.4581(2)	0.6868(4)	0.093(2)
C41	0.5132(7)	0.5701(3)	0.6409(5)	0.209(5)

Table 3.

Selected bond lengths (Å) and bond angles (°) (estimated standart deviation) for C_{41} H_{35} N_7 O_6 S_3.

S1 - O1	1.437(3)	S1 - O2	1.431(4)
S1 - N1	1.657(3)	S1 - C4	1.741(4)
S2 - O3	1.424(3)	S2 - O4	1.432(3)
S2 - N2	1.646(3)	S2 - C18	1.748(5)
S3 - O5	1.422(5)	S3 - O6	1.438(5)
S3 - N3	1.649(5)	S3 - C35	1.742(6)
N1 - C8	1.426(5)	N1 - C16	1.475(5)
N2 - C17	1.479(5)	N2 - C25	1.470(5)
N3 - C26	1.467(6)	N3 - C27	1.426(7)
N4 - C14	1.133(7)	N5 - C15	1.141(7)
N6 - C33	1.128(9)	N7 - C34	1.119(1)

O1 - S1 - O2	120.5(2)	O1 - S1 - N1	106.1(2)
O1 - S1 - C4	108.6(2)	O2 - S1 - N1	106.5(2)
O2 - S1 - C4	108.1(2)	S1 - C4 - C3	120.8(3)
N1 - S1 - C4	106.4(2)	S1 - C4 - C5	119.5(4)
O3 - S2 - O4	119.9(2)	O3 - S2 - N2	106.6(2)
O3 - S2 - C18	109.1(2)	O4 - S2 - N2	106.3(2)
N1 - C8 - C9	120.6(4)	O4 - S2 - C18	108.1(2)
N1 - C8 - C13	119.5(3)	N2 - S2 - C18	105.9(2)
O5 - S3 - O6	121.5(3)	O5 - S3 - N3	105.5(2)
O5 - S3 - C35	107.8(3)	O6 – S3 - N3	106.5(3)
O6 - S3 - C35	108.1(2)	N3 - S3 - C35	106.5(2)
S1 - N1 - C8	117.9(3)	S1 - N1 - C16	117.2(3)
C8 - N1 - C16	117.9(3)	S2 - N2 - C17	116.0(2)
N4 - C14 - C10	177.9(6)	S2 - N2 - C25	113.7(2)
N5 - C15 - C11	177.5(6)	C17 - N2 - C25	114.9(3)
N1 - C16 - C17	111.1(3)	S3 - N3 - C26	120.3(4)
N2 - C17 - C16	111.9(3)	S3 - N3 - C27	119.7(3)
S2 - C18 - C19	120.6(3)	C26 - N3 - C27	117.5(4)
S2 - C18 - C23	119.9(3)		

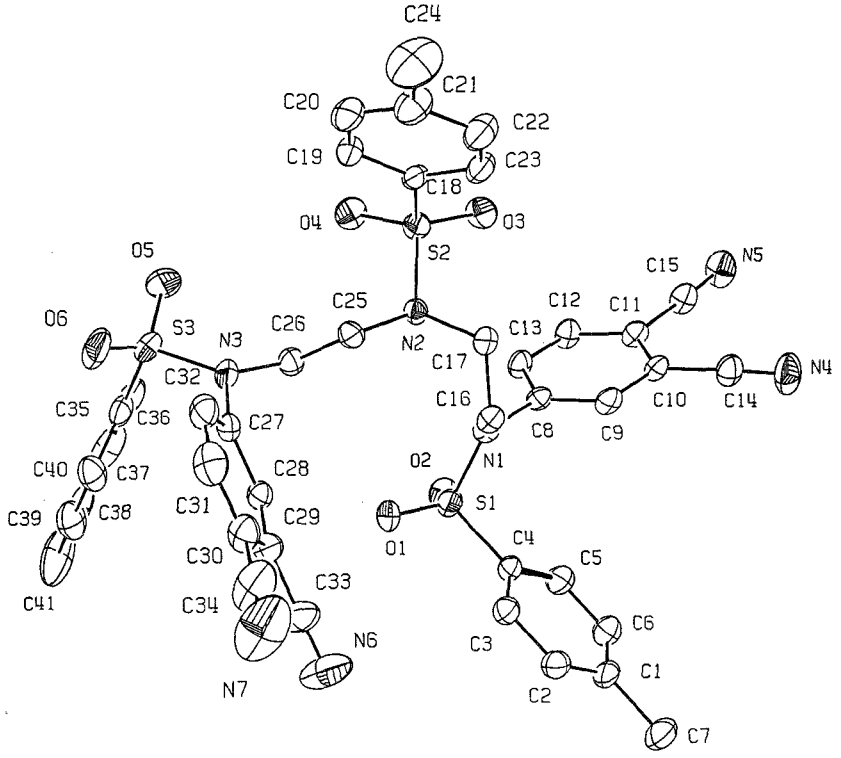


Fig. 1. The structure of title compound showing 50% probability displacement ellipsoids and atom-numbering scheme.

$I \geq 2\sigma(I)$ with a weighting scheme, $w = 1/[\sigma^2 (Fo^2) + (0.0595P)^2 + 0.0000P]$ where $P = (Fo^2+2Fc^2)/3$. The atomic coordinates and equivalent isotropic displacement parameters with estimated standard deviations for atoms except H are listed in Table - 2, and the selected bond lengths and bond angles are given Table - 3. The relative large displacement parameters for the C35-C40, C41, C24, N5 atoms can be attributed to slight disorder in these groups. Also, due to weak diffraction and poor crystal quality, R value and low resolution could not be improved further.

Results and Discussion

An ORTEP[6] drawing of the molecule with atomic numbering scheme is shown in

Table 4.

Hydrogen-bonding geometry for $C_{41}H_{35}N_7O_6S_3$ (Å, °)

D -- H .. A	D - H	H....A	D...A	D-H..A
C3 -- H3B .. O1	0.930(7)	2.587(6)	2.939(6)	103.0(5)
C9 -- H9A .. O4^{i}	0.929(6)	2.409(5)	3.324(5)	168.1(4)
C16 -- H16B .. O1	0.970(5)	2.404(5)	2.895(5)	110.9(4)
C16 -- H16B .. N5^{ii}	0.970(5)	2.609(6)	3.232(6)	122.2(4)
C17 -- H17A .. O5^{i}	0.970(5)	2.585(6)	3.351(6)	136.0(4)
C17 -- H17B .. O3	0.970(5)	2.371(5)	2.861(5)	110.7(4)
C19 -- H19A .. O4	0.930(6)	2.567(5)	2.927(6)	103.4(4)
C26 -- H26A .. O4	0.970(6)	2.501(5)	3.125(5)	122.0(4)
C26 -- H26A .. O5	0.970(6)	2.410(5)	2.880(6)	109.3(4)
C31 -- H31A .. O3^{ii}	0.929(9)	2.300(7)	3.228(7)	177.3(7)
C32 -- H32A .. O6	0.930(7)	2.536(8)	2.901(8)	103.7(6)

Symmetry codes: i = -1/2+x,1/2-y,-1/2+z, ii = -1/2+x,1/2-y,1/2+z

Table 5.

Dihedral angles formed by least-square planes for $C_{41}H_{35}N_7O_6S_3$ (°).

plane	plane	angle
I	II	44.02(1)
I	III	58.20(1)
I	IV	30.50(1)
I	V	76.58(2)
II	III	57.15(2)
II	IV	74.03(1)
II	V	59.87(2)
III	IV	64.72(2)
III	V	77.39(2)
IV	V	48.57(2)

I = C1 - C6; II = C8 - C13; III = C18 - C23; IV = C27 - C32; V = C35 - C40.

Fig. 1. The C – C bond distances and C – C – C bond angles in the five phenyl rings are in good agreement with the expected value for aromatic rings. The averege of the N≡C bond lengths,1.130(5) Å , is short enough to indicate its triplet-bond character. Also average of S - O bond lengths and O – S – O bond angles, 1.430(3) Å and 120.6(4)°, are in agreement in the similar complexes[7]. All other bond lengths and bond angles are about normal. The five phenyl rings are planar within experimental errors. The angles between the least-square planes of phenyl I, II, III, IV, V which contain C1 - C6, C8 - C13, C18 - C23, C27 - C32, C35 - C40 atoms respectively, are listed in Table - 4. C - N and CH_3 groups (except H atoms) are planar with the adjacent phenyl rings. The largest deviation from the mean planes of the molecule is 0.0129 Å for the C12 atom within the C8 - C13 plane.The crystal structure is stabilized by intra- and intermolecular C-H...O hydrogen bonds and van der Waals interactions. These bonds are listed in Table 5.

Acknowledgments

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No: 190-9609-2801. SÖ thanks the Universiti Sains Malaysia for a visiting Post Doctoral Fellowship.

References

1. Leznoff, C. C. And Lever, A. B. P., VCH, New York, 1989. Vol. 1.

2. Siemens: SMART and SAINT. Area Detector Control and Integration Software. Siemens Analytical X-ray Systems Inc., Madison, Wisconsin, USA. 1996.

3. Sheldrick, G. M. : SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany 1996.

4. Sheldrick, G.M.: SHELXS-86.Program for the solution of crystal structure. Univ.of Göttingen, Germany 1990.

5. Sheldrick, G.M.: SHELXL-97. Program for the refinement of crystal structure. Univ.of Göttingen,Germany 1998.

6. Johnson,C.K., ORTEP-III.Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, U.S.A

7. Işık,Ş., Aygun, M., Şaşmaz, S., Kendi, E., Büyükgüngör, O., Erdönmez, A., Acta Cryst., C53, 1997, 593-594.

Date Received: June 30, 1999
Date Accepted: August 30, 1999