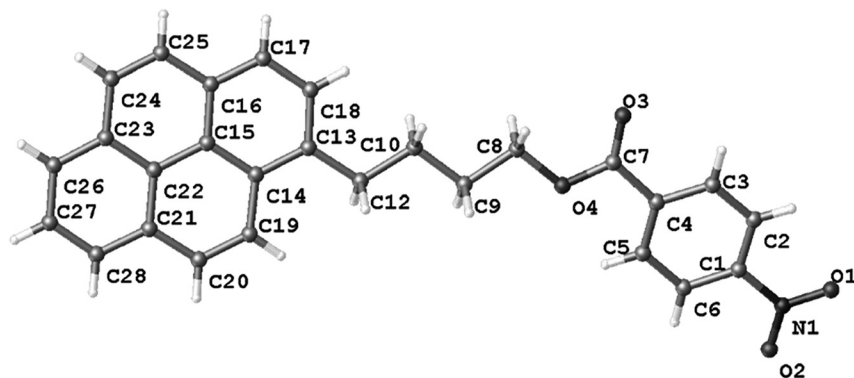


Claudio Barrientos, Juan Arturo Squella and Silvana Moris*

The crystal structure of 4-(pyren-1-yl)butyl-4-nitrobenzoate, $C_{27}H_{21}NO_4$



<https://doi.org/10.1515/ncrs-2023-0034>

Received January 20, 2023; accepted February 6, 2023;
published online February 28, 2023

Abstract

$C_{27}H_{21}NO_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.3476(2)$ Å, $b = 7.4894(2)$ Å, $c = 20.5137(5)$ Å, $\alpha = 89.3300(10)^\circ$, $\beta = 79.7070(10)^\circ$, $\gamma = 67.5220(10)^\circ$, $V = 1024.31(5)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0536$, $wR_{ref}(F^2) = 0.1792$, $T = 296.15$ K.

CCDC no.: 2240071

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

Equimolar quantities of the respective nitrobenzoyl chloride and 4-pyren-1-ylbutanol were mixed in a round bottom flask with dry THF to obtain the 4-(pyren-1-yl)butyl nitrobenzoate derivatives, according to previously reported methodology

*Corresponding author: **Silvana Moris**, Centro de Investigación de Estudios Avanzados del Maule (CIEAM), Vicerrectoría de Investigación y Postgrado, Universidad Católica del Maule, Avenida San Miguel 3605, Talca 3480112, Chile, E-mail: smoris@ucm.cl. <https://orcid.org/0000-0002-0330-8751>

Claudio Barrientos, Instituto de ciencias químicas aplicada, Facultad de Ingeniería, Universidad Autónoma de Chile, Talca, Chile

Juan Arturo Squella, Facultad de Ciencias Químicas y Farmaceuticas, Centro de Investigación de procesos redox (CiPRex), Universidad de Chile, Santiago, Chile

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.35 × 0.25 × 0.06 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	32.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	38,014, 7063, 0.040
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5031
$N(param)_{refined}$:	289
Programs:	Olex2 [1, 2], SHELX [3]

[4–6] 4-(pyren-1-yl)butyl-4-nitrobenzoate (4-NBPy) $C_{27}H_{21}NO_4$. Yellow powder, yield: 58.64%, mp: 168 °C–169 °C, ¹H NMR (CDCl₃) d (ppm): 8.22–7.76 (m, 12H, Ar–H), 4.34, (t, 2 H, CH₂–OR), 3.36, (t, 2 H, CH₂–pyrene), 2.05–1.80 (m, 4H, 2xCH₂). ¹³C-NMR (75 MHz, CDCl₃) d [ppm]: 163.62, 149.34, 134.96, 134.54, 130.39, 129.80, 129.48, 128.92, 127.57, 126.46, 126.31, 125.71, 124.91, 124.00, 123.76, 122.37, 122.15, 94.06, 64.67, 63.55, 32.00, 28.68, 27.38, 26.88. Single crystals of 4-(pyren-1-yl)butyl-4-nitrobenzoate was prepared by dissolving the polycrystalline material in boiling chloroform (0.5 mL) and then hot methanol was added dropwise (0.5 mL) [5]. The mixture was allowed to crystallize for two weeks until the appearance of yellow plates.

2 Experimental details

For solving the structure OLEX2 was used [1] with the olex2.solve [2] and refined with the use of SHELX program package [3]. SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction. H atoms were finally included in

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
O1	0.4095 (2)	0.8490 (3)	1.08666 (5)	0.0987 (5)
O2	0.6965 (2)	0.7674 (2)	1.02432 (6)	0.0892 (4)
O3	0.01850 (13)	0.67382 (17)	0.82333 (5)	0.0648 (3)
O4	0.33353 (11)	0.54604 (12)	0.76573 (4)	0.04113 (19)
N1	0.5222 (2)	0.78884 (18)	1.03367 (5)	0.0564 (3)
C1	0.44000 (19)	0.74323 (17)	0.97852 (5)	0.0437 (3)
C2	0.2401 (2)	0.7740 (2)	0.98909 (6)	0.0531 (3)
H2	0.158519	0.820771	1.030400	0.064*
C3	0.16270 (19)	0.7339 (2)	0.93679 (6)	0.0511 (3)
H3	0.027484	0.754845	0.942625	0.061*
C4	0.28751 (16)	0.66242 (16)	0.87561 (5)	0.0384 (2)
C5	0.48893 (17)	0.63062 (17)	0.86679 (5)	0.0423 (2)
H5	0.571989	0.580763	0.825928	0.051*
C6	0.56792 (19)	0.67255 (19)	0.91844 (6)	0.0465 (3)
H6	0.702598	0.653632	0.912757	0.056*
C7	0.19537 (16)	0.62925 (17)	0.81986 (5)	0.0402 (2)
C8	0.25759 (15)	0.52075 (15)	0.70760 (5)	0.0358 (2)
H8A	0.185248	0.645771	0.691641	0.043*
H8B	0.166398	0.454702	0.718498	0.043*
C9	0.43361 (14)	0.40236 (14)	0.65491 (5)	0.0328 (2)
H9A	0.502114	0.275800	0.670577	0.039*
H9B	0.527700	0.465788	0.646040	0.039*
C10	0.36291 (14)	0.37930 (14)	0.59137 (5)	0.03200 (19)
H10A	0.294305	0.506381	0.576082	0.038*
H10B	0.267575	0.317386	0.600758	0.038*
C12	0.53513 (14)	0.25967 (14)	0.53653 (4)	0.03144 (19)
H12A	0.630883	0.321344	0.528407	0.038*
H12B	0.602484	0.133206	0.552462	0.038*
C13	0.47882 (13)	0.23119 (13)	0.47123 (4)	0.02908 (18)
C14	0.62853 (13)	0.12525 (13)	0.41680 (4)	0.02766 (18)
C15	0.57399 (13)	0.09871 (13)	0.35550 (4)	0.02739 (17)
C16	0.36996 (14)	0.17924 (14)	0.34853 (5)	0.03227 (19)
C17	0.22596 (14)	0.28310 (16)	0.40299 (5)	0.0387 (2)
H17	0.091561	0.336786	0.399302	0.046*
C18	0.28016 (14)	0.30759 (16)	0.46264 (5)	0.0367 (2)
H18	0.180442	0.377396	0.498101	0.044*
C19	0.83749 (14)	0.04039 (15)	0.42073 (5)	0.0351 (2)
H19	0.876289	0.055191	0.460395	0.042*
C20	0.97964 (14)	-0.06069 (16)	0.36817 (5)	0.0390 (2)
H20	1.113403	-0.112965	0.372651	0.047*
C21	0.92887 (14)	-0.08889 (15)	0.30599 (5)	0.0349 (2)
C22	0.72401 (13)	-0.00832 (13)	0.30033 (4)	0.02965 (18)
C23	0.66812 (16)	-0.03515 (15)	0.23939 (5)	0.0347 (2)
C24	0.46044 (17)	0.04475 (17)	0.23460 (5)	0.0406 (2)
H24	0.422564	0.025098	0.195258	0.049*
C25	0.31924 (16)	0.14804 (17)	0.28639 (5)	0.0399 (2)
H25	0.185593	0.200442	0.281771	0.048*
C26	0.81792 (19)	-0.13906 (18)	0.18585 (5)	0.0450 (3)
H26	0.782881	-0.157630	0.145840	0.054*
C27	1.01746 (19)	-0.2145 (2)	0.19172 (6)	0.0508 (3)
H27	1.115145	-0.281697	0.155408	0.061*
C28	1.07376 (17)	-0.19124 (18)	0.25090 (6)	0.0458 (3)
H28	1.208538	-0.243855	0.254145	0.055*

their calculated positions and treated as riding on their parent atom with constrained thermal parameters as $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$, the constraint distances of C–H ranging from 0.93 Å to 0.97 Å.

3 Comment

The pyrene ring and derivatives are well known for their properties in photochemistry field [7]. Excited state of pyrene in solution present an excimer formation which is used as a standard for micro-environmental changes [8, 9]. Pyrene is frequently used for supramolecular studies as a probe for proteins, peptides and lipid membranes and it is very sensible to environmental changes such as pH, pressure or temperature and used to identify guest molecules, metals or other substrates [10–15]. Nitro compounds have an important role in organic synthesis due to their versatility to transform into other functional groups [16] and can be used as redox mediators for interesting biomolecules such as NADH [17]. The N–O bond lengths in the nitro group are 1.2144(16) and 1.2071(18) Å. In the crystal structure of the title compound, coplanarity of the nitro group with the pyrene group was observed (the C2–C1–N1–O1 torsion angle is 1.2(2)°).

Acknowledgements: We gratefully acknowledge support by FONDEQUIP EQM200138 for D8 Venture diffractometer.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: FONDEQUIP EQM200138.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

- Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment—Olex2 dissected. *Acta Crystallogr.* 2015, *A71*, 59–75.
- Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
- Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
- Moscoso R., Barrientos C., Moris S., Squella J. A. Electrocatalytic oxidation of NADH in a new nanostructured interface with an entrapped butylpyrene nitroaromatic derivative. *J. Electroanal. Chem.* 2019, *837*, 48–54.
- Barrientos C., Barahona P., Guevara J. L., Squella J. A., Moris S. The crystal structure of 4-(pyren-1-yl)butyl-3-nitrobenzoate, C₂₇H₂₁NO₄. *Z. Kristallogr. N. Cryst. Struct.* 2019, *234*, 1213–1214.

6. Barrientos C., Moscoso R., Moris S., Squella J. A. Electrochemical study of butyl-pyrene nitrobenzoate derivatives trapped on MWCNT nanostructured electrodes. *J. Electrochem. Soc.* 2021, *168*, 126515.
7. Figueira-Duarte T. M., Mullen K. Pyrene-based materials for organic electronics. *Chem. Rev.* 2011, *111*, 7260–7314.
8. Forster T., Kasper K. Ein Konzentrationsumschlag der Fluoreszenz des Pyrens. *Z. Elektrochem, Ber. Bunsenges. Phys. Chem.* 1955, *59*, 976–980.
9. Kalyanasundaram K., Thomas J. K. Environmental effects on vibronic band intensities in pyrene monomer fluorescence and their application in studies of micellar systems. *J. Am. Chem. Soc.* 1977, *99*, 2039–2044.
10. Sahoo D., Weers P. M. M., Ryan R. O., Narayanaswami V. Lipid-triggered conformational switch of Apolipoprotein III helix bundle to an extended helix organization. *J. Mol. Biol.* 2002, *321*, 201–214.
11. Paris P. L., Langenhan J. M., Kool E. T. Probing DNA sequences in solution with a monomer-excimer fluorescence color change. *Nucleic Acids Res.* 1998, *26*, 3789–3793.
12. Tong G., Lawlor J. M., Tregear G. W., Haralambidis J. Oligonucleotide-polyamide hybrid molecules containing multiple pyrene residues exhibit significant excimer fluorescence. *J. Am. Chem. Soc.* 1995, *117*, 12151–12158.
13. Song X., Swanson B. I. Rational design of an optical sensing system for multivalent proteins. *Langmuir* 1999, *15*, 4710–4712.
14. Pokhrel M. R., Bossmann S. H. Synthesis, characterization, and first application of high molecular weight polyacrylic acid derivatives possessing perfluorinated side chains and chemically linked pyrene labels. *J. Phys. Chem. B* 2000, *104*, 2215–2223.
15. Ludwig R., Dzung N. T. K. Calixarene-based molecules for cation recognition. *Sensors* 2002, *2*, 397–416.
16. Yan G., Yang M. Recent advances in the synthesis of aromatic nitro compounds. *Org. Biomol. Chem.* 2013, *11*, 2554–2566.
17. Contreras G., Barrientos C., Moscoso R., Álvarez-Luejic A., Squella J. A. Electrocatalytic determination of NADH by means of electrodes modified with MWCNTs and nitroaromatic compounds. *Microchem. J.* 2020, *159*, 105422.