Pergamon

Tetrahedron Letters 42 (2001) 3855–3856

TETRAHEDRON
LETTERS

Synthesis and X-ray crystal structure of spiro[3.3]heptane-2,6-dispirofluorene

Olivier Pons Y. Moll, Thierry Le Borgne, Pierre Thuéry and Michel Ephritikhine*

Service de Chimie Moléculaire, DRECAM, DSM, CNRS URA 331, CEA Saclay, 91191 Gif-sur-Yvette, France

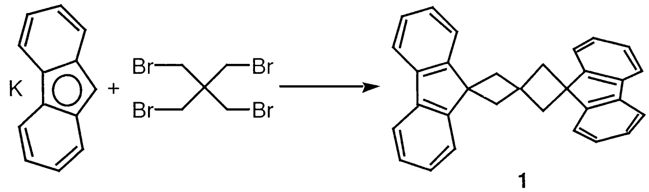
Received 18 January 2001; accepted 13 April 2001

Abstract—Reaction of pentaerythrityl tetrabromide with fluorenyl potassium gave the title compound in 53% yield. The crystal structure revealed that in this unique trispiro[4.1.1.4.1.1]pentadecatetraene derivative, the adjacent rings are planar and orthogonal. © 2001 Elsevier Science Ltd. All rights reserved.

Reactions of 1,3-dibromides or 1,3-ditosylates with alkali metal salts of malonate esters have been extensively used for the preparation of spiro or polyspiro linkages with four-membered rings.[1] The spiro[3.3]heptane-2,6-dicarboxylic acid, the Fecht acid, was thus synthesised by reaction of pentaerythrityl tetrabromide with the sodium salt of dimethyl malonate.[2] This type of reaction has been much developed by Buchta et al. who prepared a series of homologous compounds containing up to ten cyclobutane rings,[3] whereas the Fecht acid was the precursor of a number of spiro[3.3]heptane derivatives that are interesting for their structure and reactivity.[4,5] However, the preparation of spirocyclic molecules by reaction of 1,3-dibromides or 1,3-ditosylates with active methylene groups other than malonate esters seems to have been neglected. Here, we report the synthesis and X-ray crystal structure of such a compound, the spiro[3.3]heptane-2,6-dispirofluorene **1**.

Compound **1** was prepared by treatment of pentaerythrityl tetrabromide with the lithium or potassium salt of the fluorenyl anion (Scheme 1). The reaction was complete after 10 h at 65°C and, following usual work-up and crystallisation from dichloromethane, **1** was isolated as colourless microcrystals in 53% yield. The one-step synthesis of the trispiro compound **1** is remarkable, being in contrast to the reaction of fluorenyl lithium with 1,3-propanediol-ditosylate, which gave a mixture of mono- and disubstitution products, without formation of a cyclobutane derivative.[6]

Compound **1** is a unique example of a trispiro[4.1.1.4.1.1]pentadecatetraene molecule; its crystal structure is represented in Fig. 1. The molecule has a crystallographically imposed S_4 symmetry, the central spiro carbon C1 being located on the inversion centre and the other spiro carbon C3 lying on the two-fold axis. As a consequence, the two identical cyclobutane rings are planar and orthogonal; these form quite perfect squares with a mean C–C–C angle of 90.0(6)°. This geometry differs markedly from that found so far in spiro[3.3]heptane derivatives where the four-membered rings adopt invariably a puckered conformation.[4] The planar fluorene moiety (within ±0.042 Å) and the adjacent cyclobutane ring are almost perpendicular, with a dihedral angle of 87.3(3)°. Such an alternate orthogonal arrangement of a polyspirane compound is, to our knowledge, unprecedented.[7] The C–C bond lengths are unexceptional; as already noted, C–C bonds in cyclobutane rings are longer, with a mean value in **1** of 1.554(5) Å, than C–C bonds in less-strained carbocycles.[8]



1

Scheme 1.

Keywords: spiro compounds; cyclobutanes; fluorenes; X-ray crystallography.

* Corresponding author. E-mail: ephri@drecam.cea.fr

PII: S0040-4039(01)00610-4

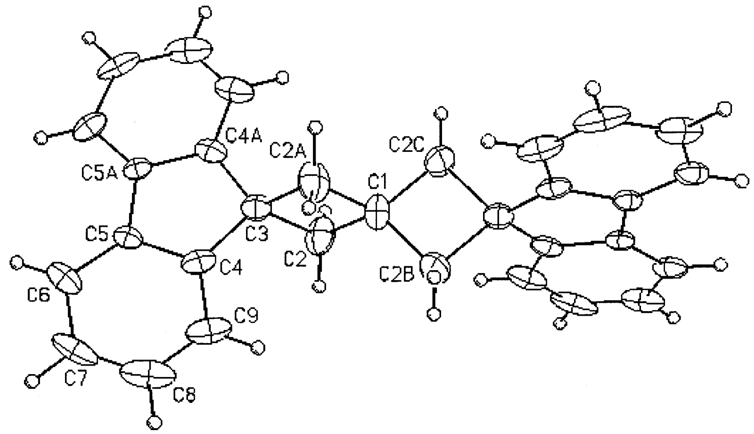


Figure 1. Crystal structure of **1**. Ellipsoids drawn at the 20% probability level. Selected bond distances (Å) and angles (°): C1–C2 1.550(5), C2–C3 1.557(6), C3–C4 1.489(5), C4–C5 1.392(5), C5–C5A 1.466(6), C2–C1–C2A 89.7(3), C2–C1–C2B 120.15(16), C1–C2–C3 90.5(3), C2–C3–C2A 89.3(5), C4–C3–C4A 101.5(4), C2–C3–C4 117.3(3). Symmetry codes A: 1–*x*, –*y*, *z*; B: 1/2+*y*, 1/2–*x*, 1/2–*z*; C: 1/2–*y*, *x*–1/2, 1/2–*z*.

Experimental

1,2,3,4,10,11,12,13-Tetrabenzotrispiro[4.1.1.4.1.1]pentadeca-1,3,10,12-tetraene 1: To a suspension of fluorenyl potassium (404 mg, 1.98 mmol) in dry tetrahydrofuran (25 ml) was added the tetrabromide $C(CH_2Br)_4$ (171 mg, 0.44 mmol). The mixture was stirred for 10 h at 65°C. The orange solution was evaporated to dryness and the residue hydrolysed with H_2O (20 ml). The reaction mixture was extracted with CH_2Cl_2 (2×15 ml). The combined organic phases were washed subsequently with brine and H_2O. After drying (Na_2SO_4) and removal of the solvent, the crude product was crystallised from CH_2Cl_2 and was isolated as colourless crystals (92 mg, 53%), mp 350–353°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.73–7.62 (m, 8H, Ph), 7.37–7.25 (m, 8H, Ph), 3.07 (s, 8H, CH_2). Anal. calcd for $C_{31}H_{24}$: C, 93.94; H, 6.06. Found: C, 93.74; H, 6.04.

X-ray structural analysis of compound 1. Crystal data: $C_{31}H_{24}$, $M=396.50$, tetragonal, $I\bar{4}2d$, $a=10.4554(15)$, $c=19.416(2)$ Å, $V=2122.5(5)$ Å^3, $Z=4$, $D_c=1.241$ g cm^{-3}, μ(Mo Kα) 0.070 mm^{-1}, $F(000)=840$, $T=110(2)$ K. The data were collected on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and subsequent Fourier-difference syntheses and refined by full-matrix least-squares on F^2 with SHELXTL.[9] Carbon atoms were refined anisotropically and hydrogen atoms were introduced at calculated positions as riding atoms, with an isotropic displacement parameter equal to 1.2 times that of the parent atom. $R_1=0.062$, $wR_2=0.146$, $S=1.049$ for 918 unique reflections ($R_{int}=0.067$) and 72 parameters. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 156367. Copies of the data can be obtained, free of charge, on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

The authors would like to thank Dr. C. Villiers for helpful discussions.

References

1. Krapcho, A. P. *Synthesis* **1974**, 383.
2. (a) Fecht, H. *Chem. Ber.* **1907**, *40*, 3888; (b) Backer, H. J.; Schurink, H. B. J. *Recl. Trav. Chim. Pays Bas* **1931**, *50*, 921.
3. Buchta, E.; Merk, W. *Liebigs Ann. Chem.* **1966**, *694*, 1.
4. (a) Wynberg, H.; Houbiers, J. P. M. *J. Org. Chem.* **1971**, *36*, 834; (b) Hulshof, L. A.; Vos, A.; Wynberg, H. *J. Org. Chem.* **1972**, *37*, 1767; (c) Hulshof, L. A.; Wynberg, H.; van Dijk, B.; de Boer, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 2733; (d) Potenza, J. A.; Kukkola, P. J.; Knapp, S.; Schugar, H. J. *Acta Crystallogr.* **1990**, *C46*, 2401; (e) Harada, N.; Soutome, T.; Murai, S.; Uda, H. *Tetrahedron: Asymmetry* **1993**, *4*, 1755.
5. (a) Roberts, C.; Walton, J. C.; Maillard, B. *J. Chem. Soc., Perkin Trans. 2* **1986**, 305; (b) Tang, H.; Baba, M.; Imae, I.; Kawakami, Y. *Polym. J.* **1999**, *31*, 313; (c) Tang, H.; Miura, H.; Imae, I.; Kawakami, Y. *Polym. J.* **1999**, *31*, 1041.
6. Fritze, C.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **1995**, *501*, 41.
7. A dispiro[5.2.5.2]hexadecane with a linear molecular shape has been reported: Feuerbacher, N.; Vögtle, F.; Windscheidt, J.; Poetsch, E.; Nieger, M. *Synthesis* **1999**, 117.
8. Adman, E.; Margulis, T. N. *J. Am. Chem. Soc.* **1968**, *90*, 4517.
9. Sheldrick, G. M. SHELXTL, Version 5.1; University of Göttingen: Germany, 1999. Distributed by Bruker AXS, Madison, WI, USA.