Crystal structures of two rubrene derivatives

PAUL SCHERRER INSTITUT

Götz Schuck [a], Simon Haas [b], Ulrich Berens [c] and Hans-Jörg Kirner [c]

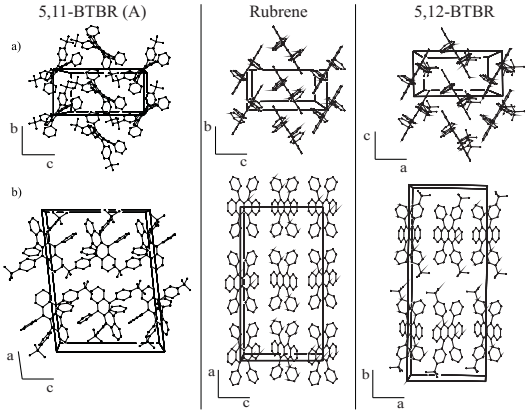
[a] Laboratory for Neutron Scattering ETH Zürich & PSI, Villigen, Switzerland, [b] ETH Zürich, Switzerland, [c] Ciba Specialty Chemistry Inc., 4002 Basel, Switzerland

Single crystal structure refinement of 5,11-BTBR (A) and 5,12-BTBR

5,11-bis-(4-tert-butyl-phenyl)-6,12-diphenyl-naphthacene (5,11-BTBR) is a derivate of rubrene with two polymorphs (A and B) where t-butyl sidegroups are added.

5,11-BTBR Polymorph A has a structure drastically different from the packing of unsubstituted rubrene with enhanced backbone-backbone spacing between two molecules [2]. Remarkably, the naphthacene backbone of the molecules is significantly twisted in polymorph A, with a twist angle of 43° between the two opposite C-C bonds at both ends of the backbone. The resulting backbone-backbone distances are not shorter than 4.36 Å, which is commonly expected to drastically reduce the π-π * overlap.

In the case of 5,12-bis-(4-tert-butyl-phenyl)-6,11-diphenyl-naphthacene (5,12-BTBR) [3], the in-plane arrangement of the molecules is very similar to that of rubrene [4], with even shorter distances between the naphthacene backbones (3.62 Å compared to 3.75 Å). However, the addition of the t-butyl groups increases the inter-layer spacing by 31%. Interestingly, it leaves the backbone almost perfectly planar.

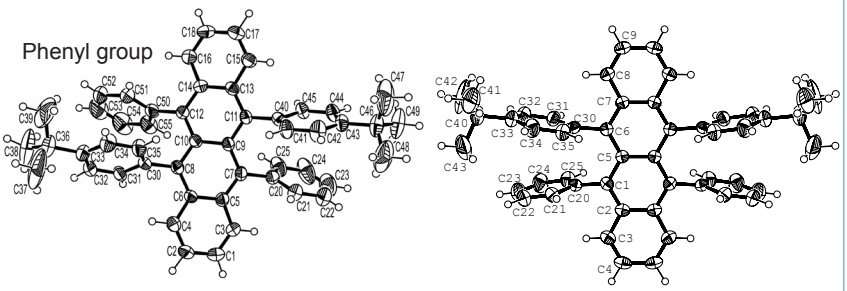


Above: Perspective views of the structures of 5,11-BTBR (polymorph A, left) [2], rubrene at 293 K (center) [4], and 5,12-BTBR [3] (similar to 5,11-BTBR polymorph B, right).

5,11-BTBR (A) 5,12-BTBR

Tetracene backbone

Phenyl group



SHELXL refinement from Siemens SMART CCD data

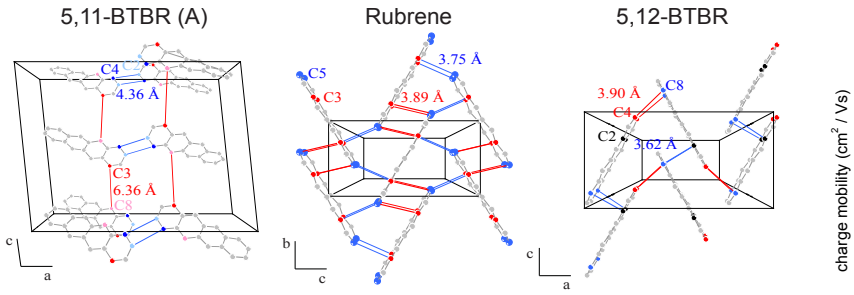
5,11-BTBR (A); $C_{50}H_{44}$; M_r = 644.85 [2]	
Space group	Monoclinic, $P2_1/c$
a,b,c (Å); β (°)	23.527 (3) 9.0277 (10) 17.764 (2) 95.928 (4)
V (Å³)	3752.8 (8)
Exposure (sec)	5
Z	4
Reflections	31129
Unique reflec.	6626
Reflections with I > 2σ(I)	3478
Parameters; Ratio	536; 12.4
Mean σ(C-C) (Å)	0.007
R_{int}	0.100
R	0.098
$_wR$	0.169
S	1.11

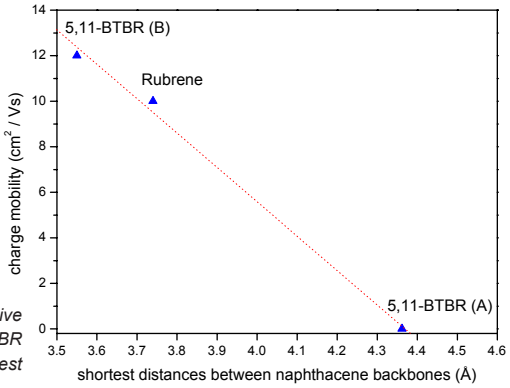
5,12-BTBR; $C_{50}H_{44}$; M_r = 644.90 [3]	
Space group	Orthorhombic, Pnma
a,b,c (Å)	14.158 (2) 35.390 (5) 7.2215 (11)
V (Å³)	3618.4 (9)
Exposure (sec)	5
Z	4
Reflections	28135
Unique reflec.	3446
Reflections with I > 2σ(I)	2208
Parameters; Ratio	282; 12.2
Mean σ(C-C) (Å)	0.005
R_{int}	0.0298
R	0.074
$_wR$	0.207
S	1.15

The structure of polymorph 5,11-BTBR (B) could not be solved so far, as the material seems to exclusively grow as ultrathin platelets. From measurements of the d-spacing perpendicular to the extended crystal surface [1], a structure closely related to the one found for a constitutional isomer, 5,12-bis-(4-tert-butyl-phenyl)-6,11-diphenyl-naphthacene was assumed for polymorph B.

Charge mobility vs. intermolecular π-orbital overlap

The electric transport properties of the two polymorphs are completely different: in polymorph B the in-plane hole mobility of 12 cm^2/Vs measured on single crystal FETs is just as high as in rubrene crystals, whereas polymorph A does not show any measurable field-effect [1].





Above: Intermolecular π-orbital overlap. Structural details: just naphthacene backbones are shown. Perspective views of 5,11-BTBR (polymorph A, left), rubrene at 293 K (center) [4], and 5,12-BTBR (similar to 5,11-BTBR polymorph B, right). Right: charge mobility [1] vs. shortest intermolecular π-orbital overlap [2,3,4]; the shortest intermolecular π-orbital overlap of 5,11-BTBR (B) is represented by C2-C8 of 5,12-BTBR

Reference: [1] Haas, S., Stassen, A. F., Schuck, G., Pernstich, K. P., Gundlach, D. J., Batlogg, B., Berens, U. & Kirner, H. J. (2007). Phys. Rev. B. Accepted. (cond-mat, arXiv:0707.0461); [2] G. Schuck, S. Haas, A. F. Stassen, U. Berens and B. Batlogg, Acta Cryst. (2007). E63, o2894; [3] G. Schuck, S. Haas, A. F. Stassen, H.-J. Kirner and B. Batlogg, Acta Cryst. (2007). E63, o2893; [4] O. D. Jurchescu, A. Meetsma and T. T. M. Palstra, Acta Cryst. (2006). B62, 330-334

EMAIL: goetz.schuck@psi.ch • WWW: http://b-net.de/schuck/rubrene