Молекулярные структуры димеров диамантила и оксадиамантила:

экспериментальное и теоретическое исследование

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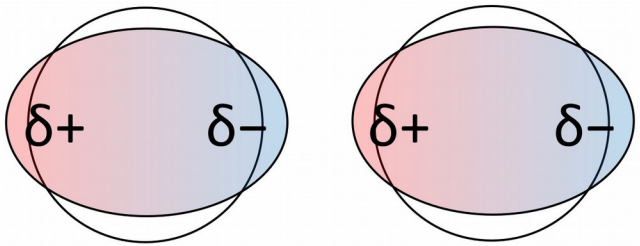
Онлайн-симпозиум по вычислительной химии памяти А. А. Грановского
13-14 апреля 2020

Дисперсионное взаимодействие

Пример 1

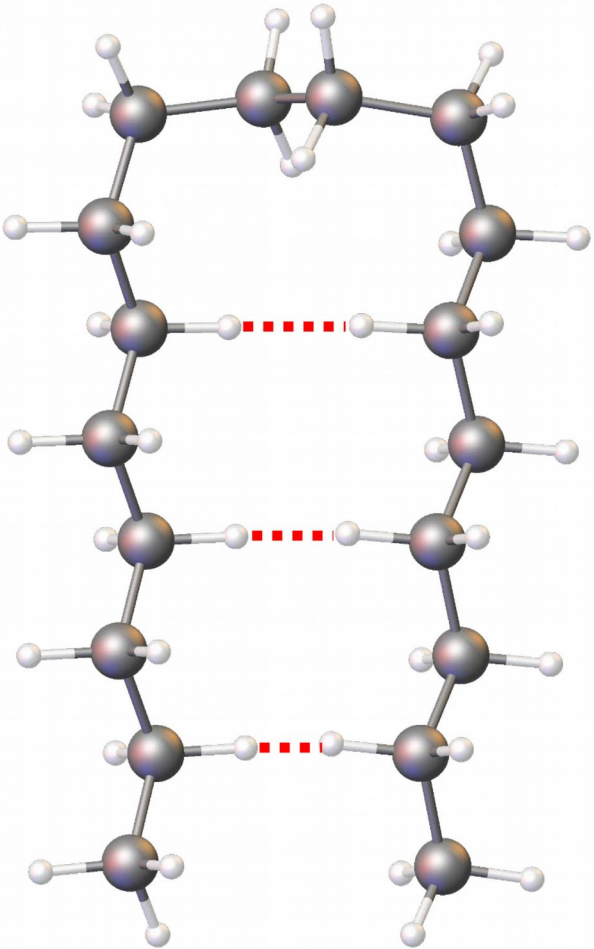


$E < 10$ kJ mol^{-1}

hydrogen bonds

$E \approx 40$ kJ mol^{-1}

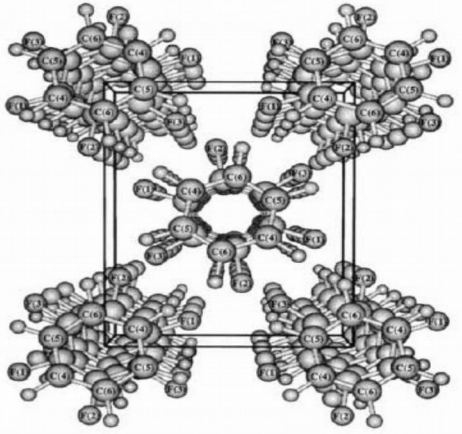
	boiling point / K[1]
He	4
Ne	27
Ar	87
Kr	120
Xe	165

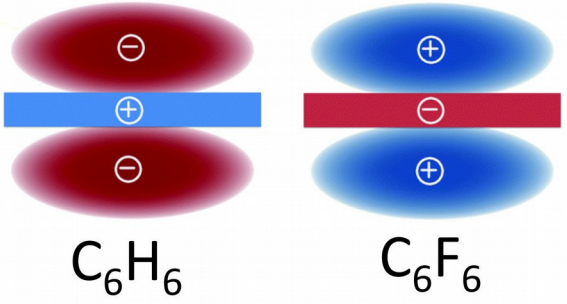


[1] GESTIS Stoffdatenbank, http://gestis.itrust.de.
[2] N. O. B. Lüttschwager, T. N. Wassermann, R. A. Mata, M. A. Suhm, *Angew. Chem. Int. Ed*. **2013**, *52*, 463 – 466.

Пример 2

	m.p. / °C[6]
C_6H_6	6
C_6F_6	4
C_6H_6:C_6F_6 (1:1)	24





π-stacking in general[9]

magnitude: dispersion

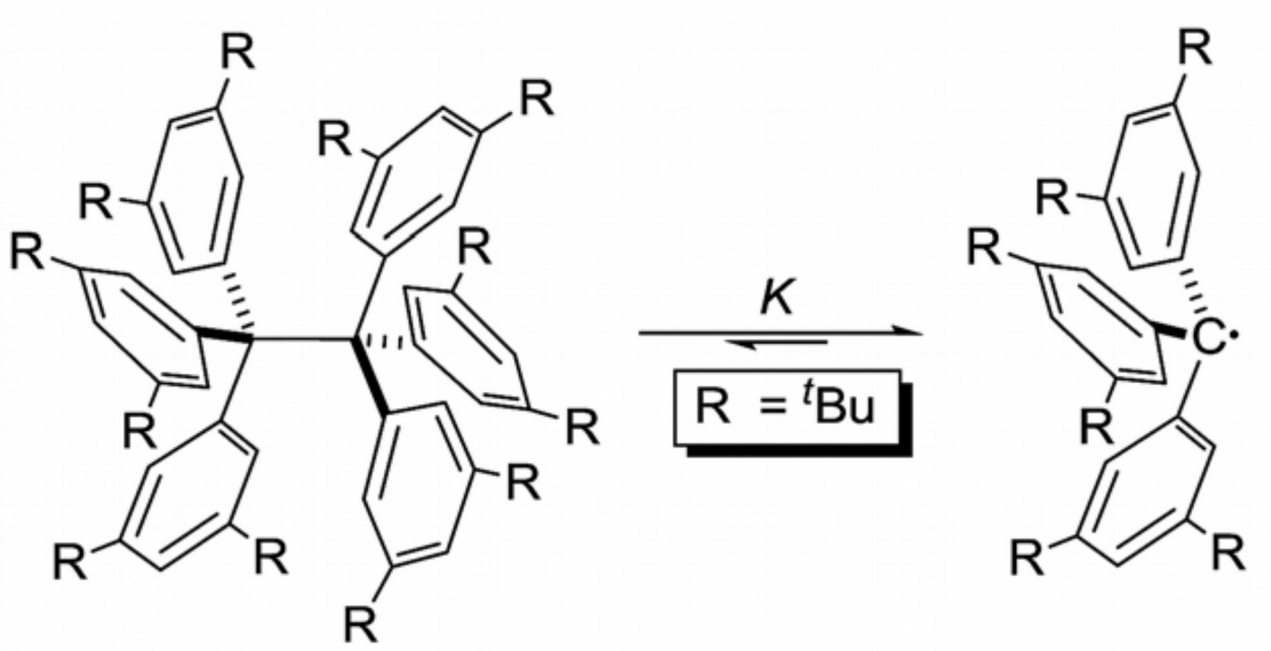
substituent effects: electrostatic

C_6H_6–C_6F_6 dimer[10]

major source of attraction: dispersion

[6] C. R. Patrick, G. S. Prosser, *Nature* **1960**, *187*, 1021.
[7] J. H. Williams, J. K. Cockcroft, A. N. Fitch, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1655 – 1657.
[8] C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa, P. M. Deya, *Chem. Phys. Chem.* **2003**, *4*, 1344 – 1348.
[9] M. O. Sinnokrot, C. D. Sherrill, *J. Am. Chem. Soc.* **2004**, *126*, 7690 – 7697.
[10] S. Tsuzuki, T. Uchimaru, M. Mikami, *J. Phys. Chem. A* **2006**, *110*, 2027 – 2033.

Пример 3

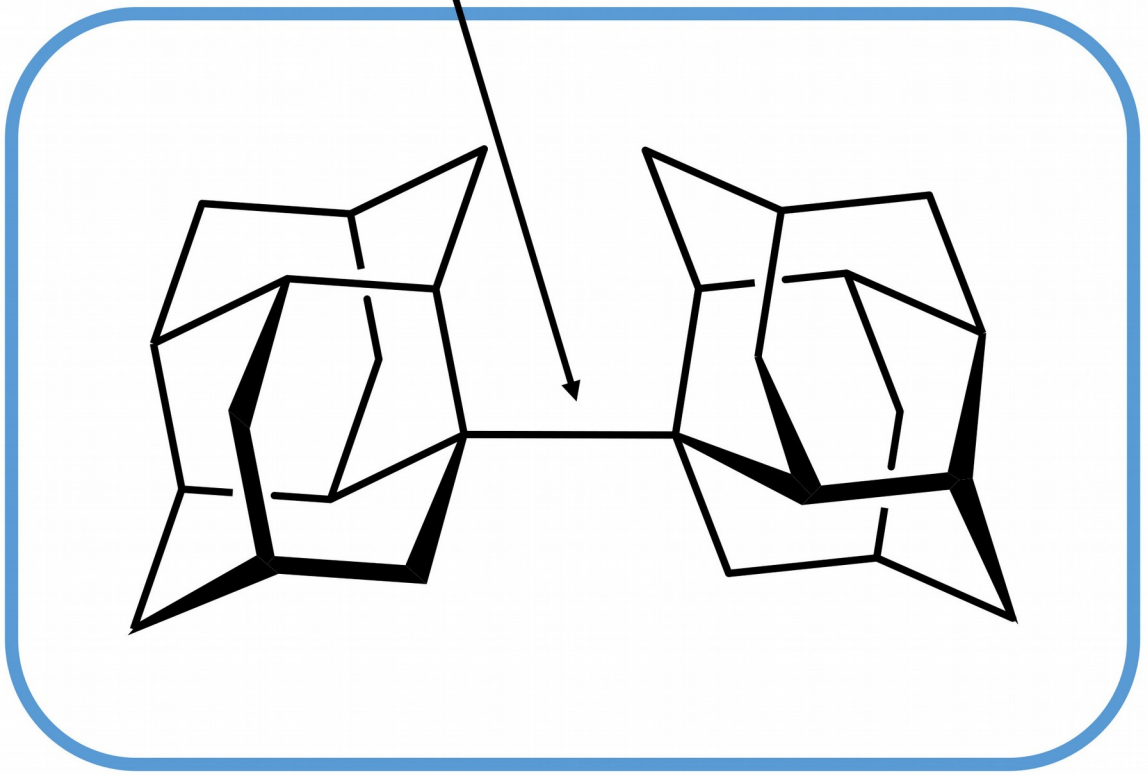


S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.*, 2016, 8(1), 405–410.

Димеры диамантила и оксадиамантила

Димер диамантила

XRD: 1.647(2) Å[3] ↔ propane: 1.521(1) Å[4]

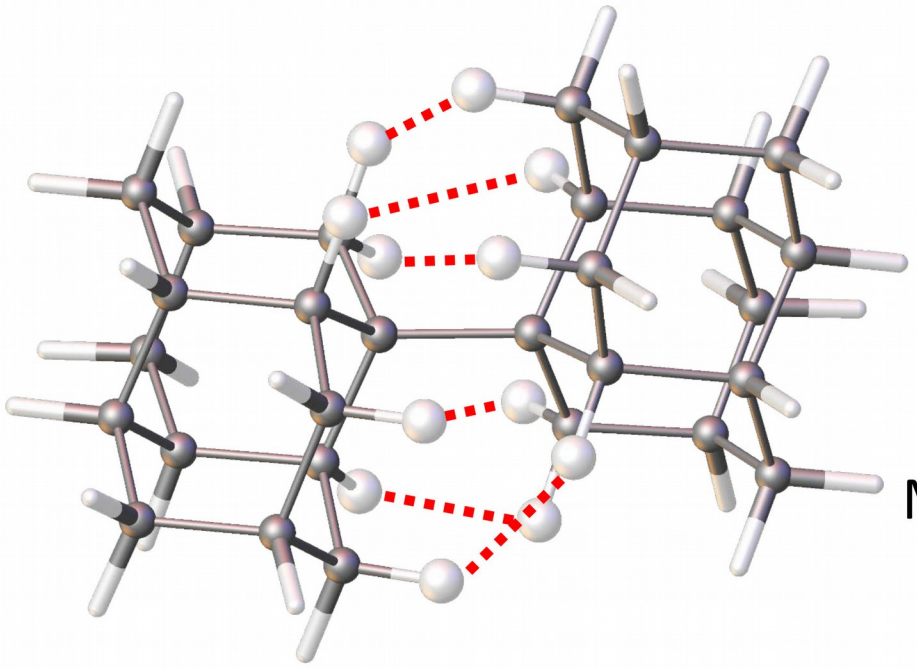


stable up to
350 °C

[3] P. R. Schreiner, L. V. Chernish, P. A. Gunchenko, E. Yu. Tikhonchuk, H. Hausmann, M. Serafin, S. Schlecht, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin, *Nature* **2011**, *477*, 308 – 311.

[4] R. Boese, H.-C. Weiss, D. Bläser, *Angew. Chem.* **1999**, *38*, 988 – 992.

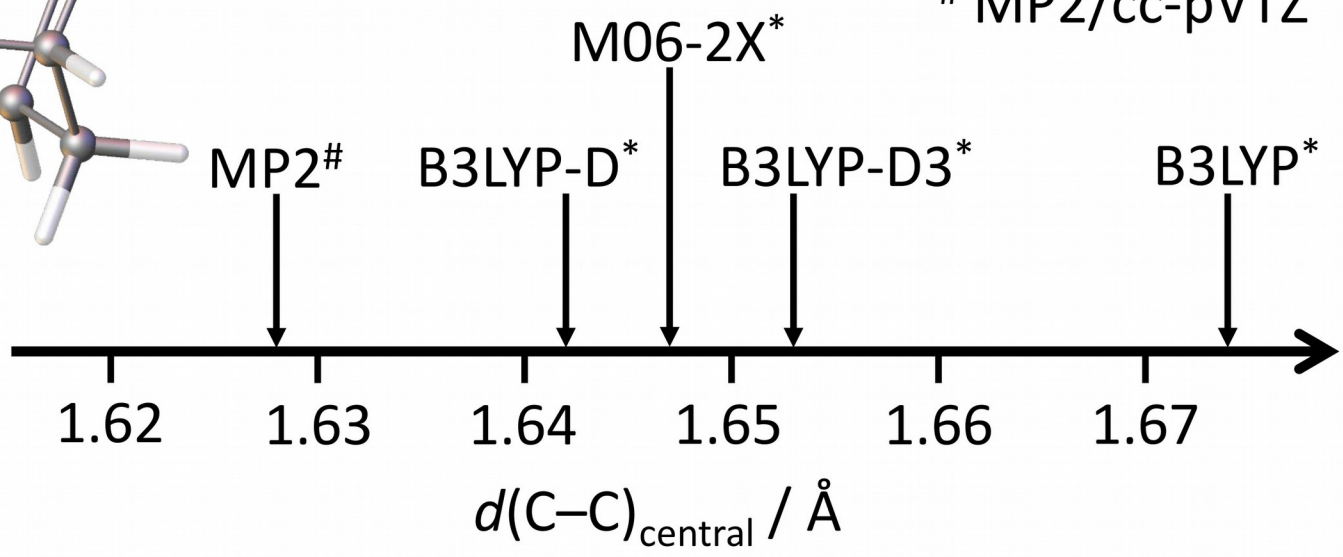
КХ расчеты



Ш. Гриммэ: PBEh-3c !???

* DFT/cc-pVDZ[5]

\# MP2/cc-pVTZ

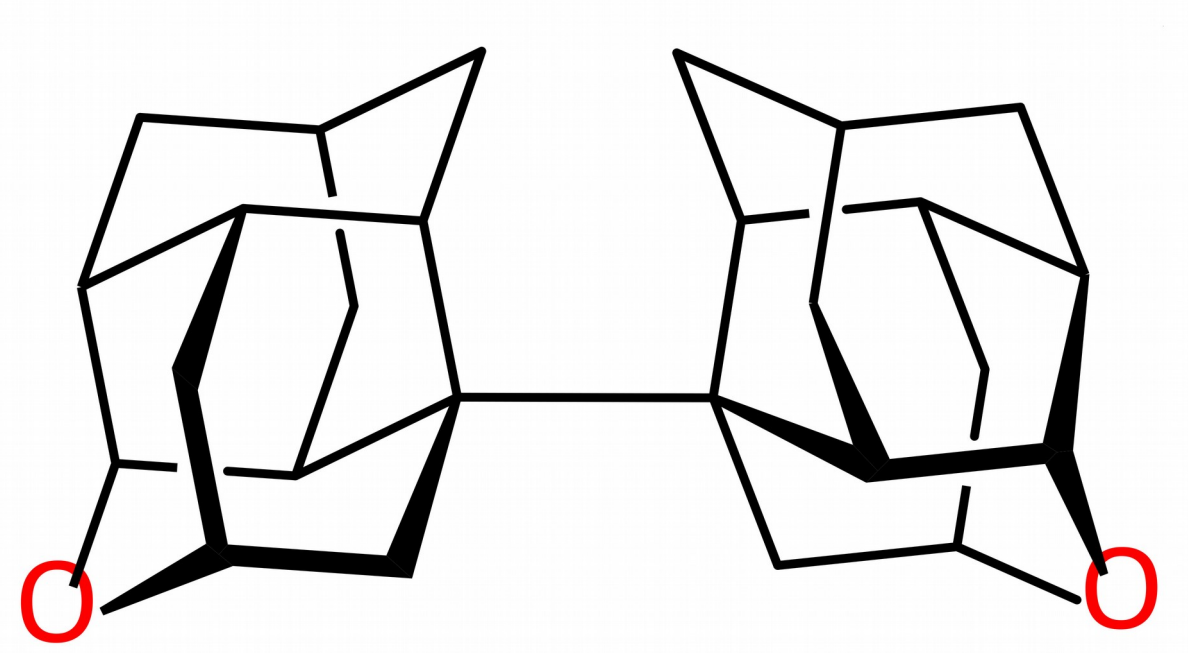


GED → benchmark

[5] A. A. Fokin, L. V. Chernish, P. A. Gunchenko, E. Yu. Tikhonchuk, H. Hausmann, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, P. R. Schreiner, *J. Am. Chem. Soc.* **2012**, *134*, 13641 – 13650.

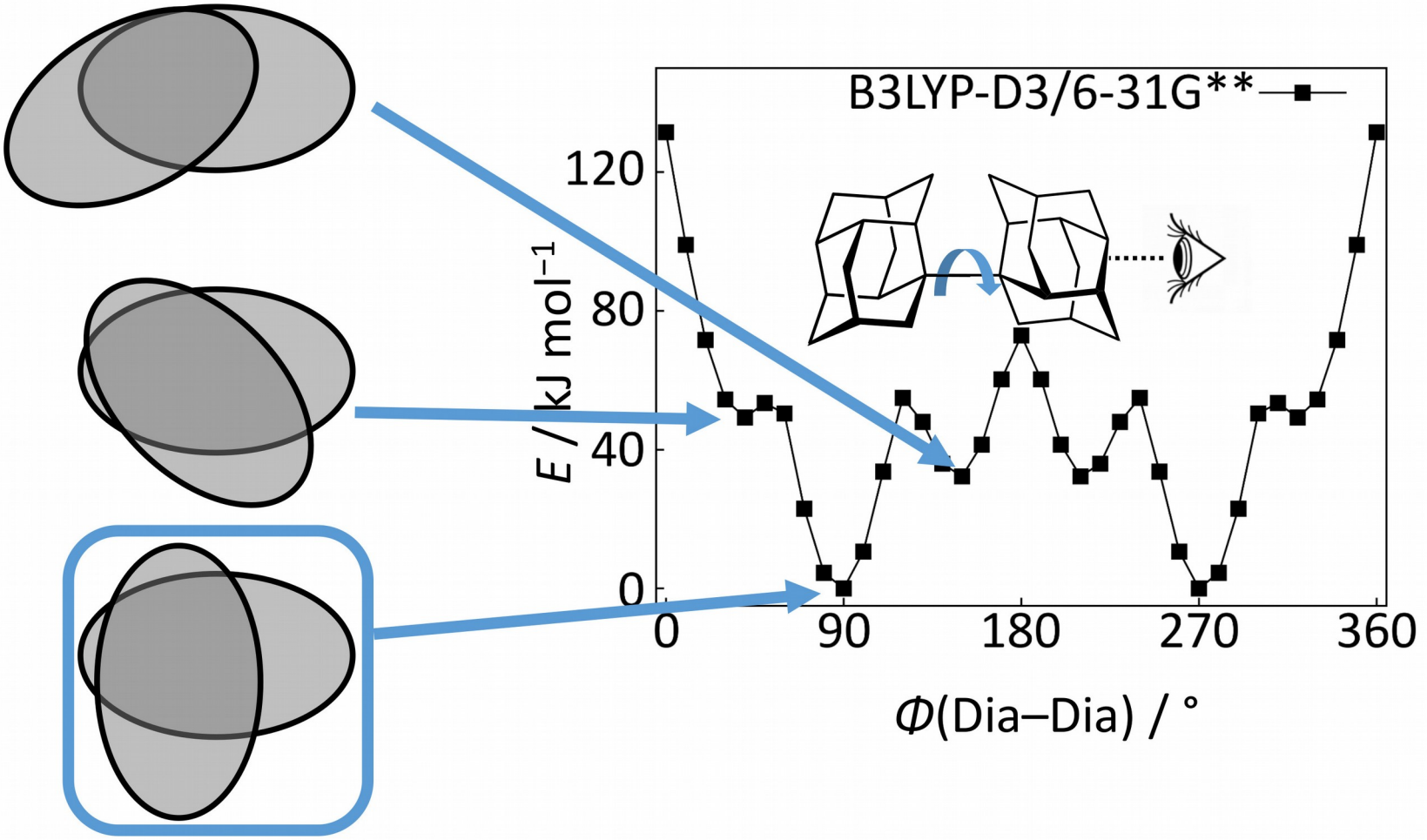
Новое вещество

6,6'-бис-(3-оксадиамантан)



+ Возможность снять МВ спектры

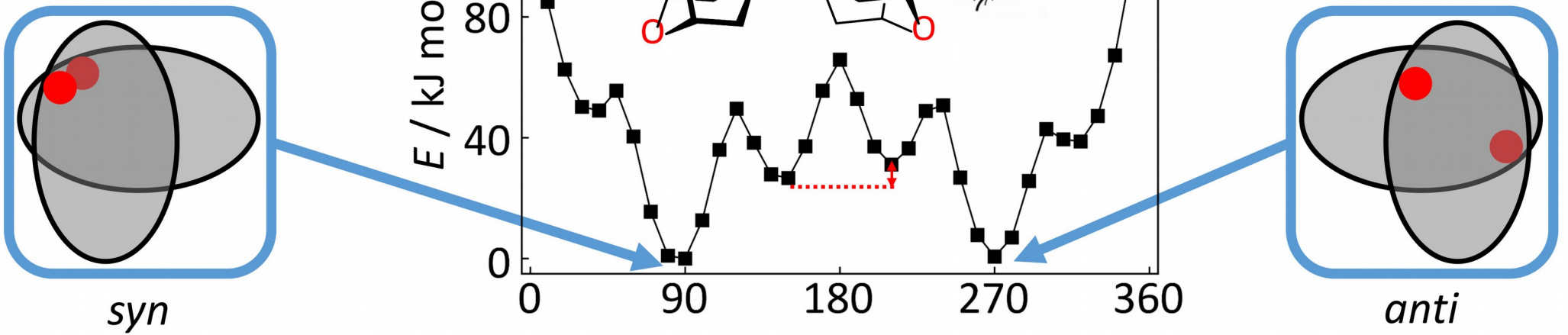
Потенциал 1



T = 583 K

χ = 99 %

Потенциал 2



$\Delta E_{syn-anti}$ = 1.2 kJ mol^{-1}

→ 2 conformer model

additional parameters:

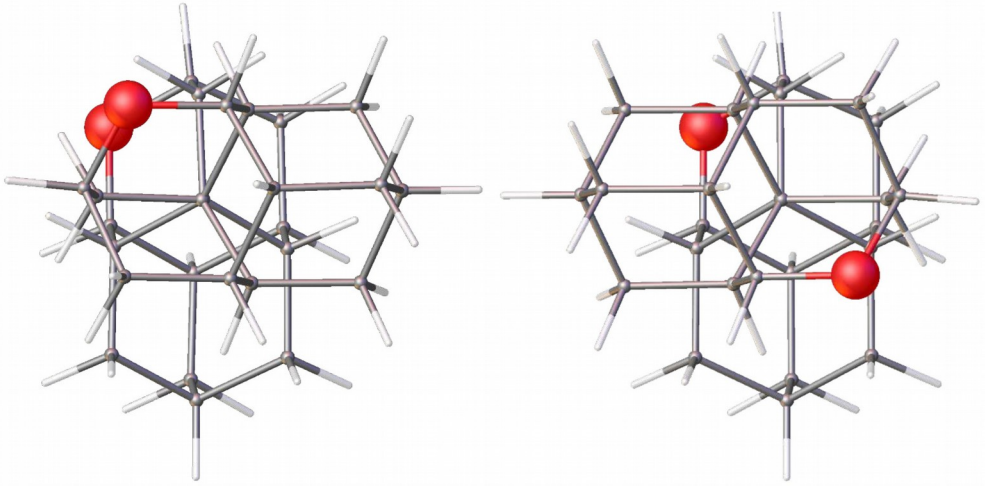
- d(C–O)
- Φ_2(Dia–Dia)
- $\chi_{syn:anti}$

Микроволновая спектроскопия

syn

$\mu_A = \mu_B = 0$ D

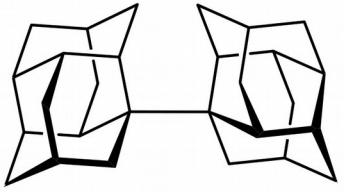
$\mu_C = 2.5$ D*



anti

$\mu_A = \mu_B = 0$ D

$\mu_C = 0.4$ D*



$\mu_A = \mu_B = 0$ D

$\mu_C = 0.05$ D*

*PBEh-3c

rotational constants

$A = 396.3518(1)$ MHz

$B = 158.91216(8)$ MHz

$C = 158.83150(8)$ MHz

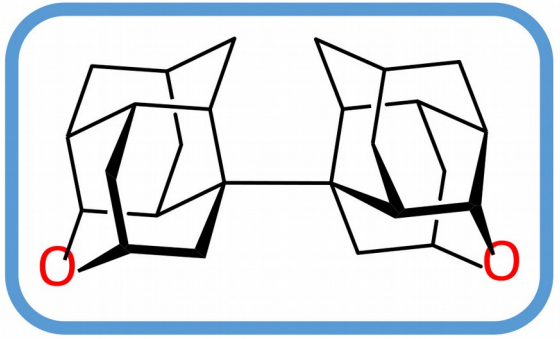
MW → B_0 → B_e ↘

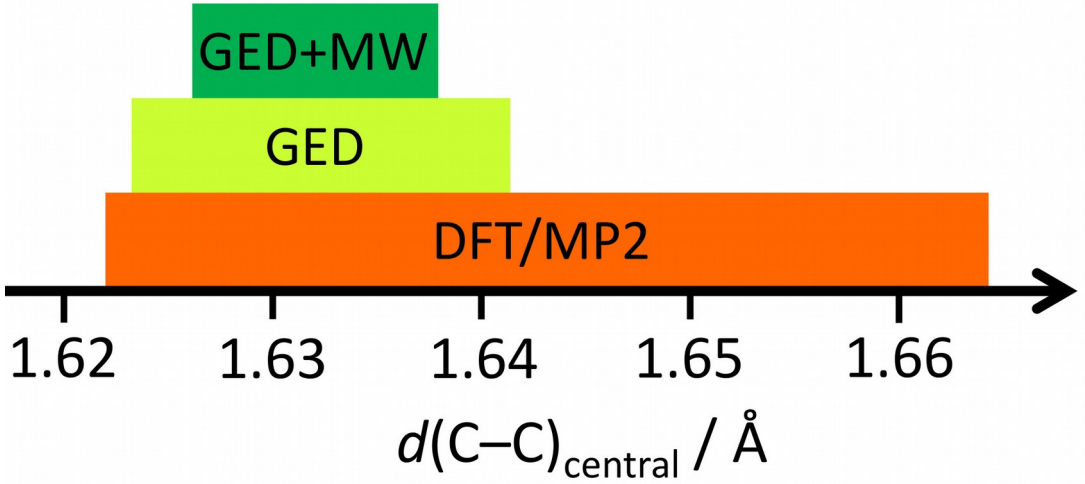
GED → r_a → r_e ↗

GED+MW structure refinement

Газовая электронография в Билефельде

Результаты: *JACS*, 56 (2017) 9619





Firefly 8.1.1, Linux, MPICH1, 40 нод →

Метод	Окса-димер	Димер
XRD	1.643(1)	1.647(4)
GED	1.632(9)	**1.630(5)**
GED+MW	**1.632(5)**	-
B3LYP/cc-pVTZ	1.662	1.674
TPSS/cc-pVTZ	1.658	1.668
HF/cc-pVTZ	1.652	1.664
B97-D3/cc-pVTZ	1.651	1.662
B3PW91/cc-pVTZ	1.646	1.657
TPSS-D3/cc-pVTZ	1.642	1.652
B3LYP-D3/cc-pVTZ	1.642	1.653
ωB97XD/cc-pVTZ	1.638	1.648
PBE0/cc-pVTZ	1.637	1.648
M06-2X/cc-pVTZ	1.636	1.647
PBEh-3c	**1.632**	1.642
SCS(1.2;2/3)-MP2/def2-QZVP	1.629	1.640
PBE0-D3/cc-pVTZ	1.628	1.638
B3PW91-D3/cc-pVTZ	1.627	1.636
PW6B95-D3/def2-QZVP	1.626	1.636
ae-MP2/cc-pwCVTZ	1.622	**1.633**

Спасибо* за внимание!

* Dr. Sebastian Blomeyer за картинки и слайды.