

Теоретические основы органической ХИМИИ

Соединения с инвертированной геометрией

Лекция 4 (мультимедийный курс)

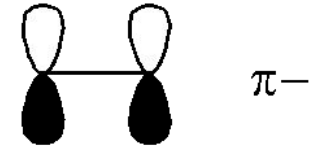
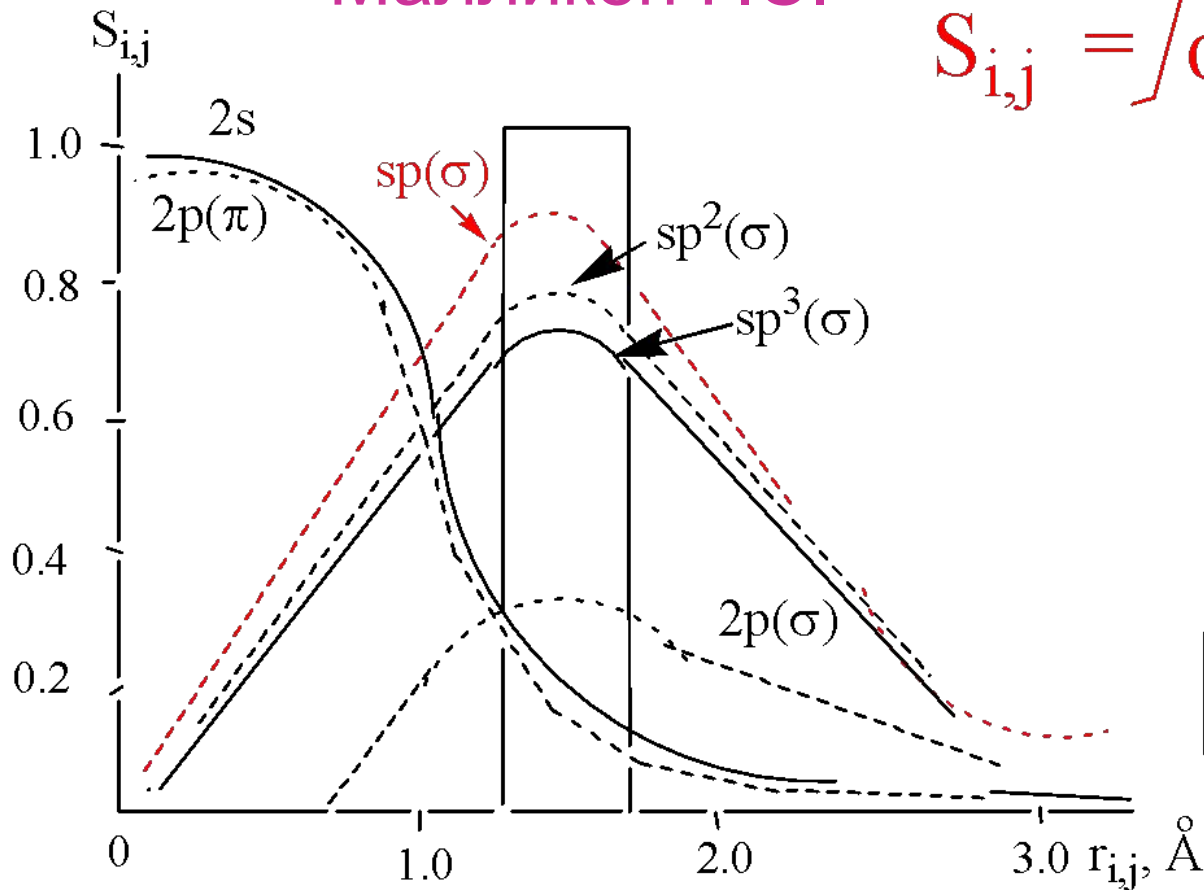
Проф. Бородкин Г.И.

Теория гибридизации

1. Направленность орбиталей
2. Принцип максимального орбитального перекрывания

Малликен Р.С.

$$S_{i,j} = \int \phi_i \phi_j d\tau$$

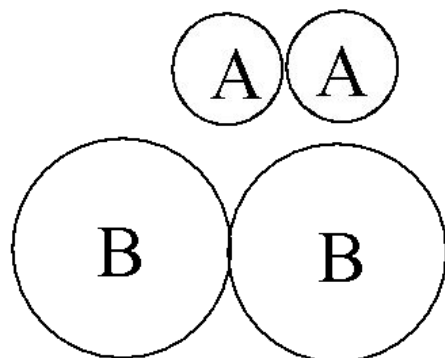
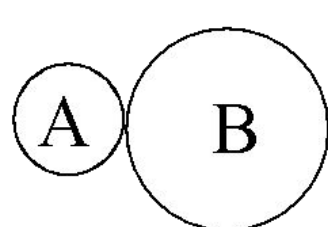


$$sp^3 < sp^2 < sp$$

Молекула	Гибридизация	E_{C-H} , ккал/моль	l_{C-H} , Å
CH_3-CH_3	sp^3	97	1.094
$CH_2=CH_2$	sp^2	104	1.084
$CH\equiv CH$	sp	114	1.061

ПМП ! прочность связи ↑ укорочение ↓

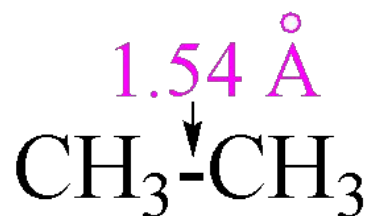
Ковалентный радиус



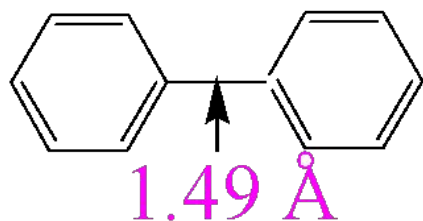
$$r_A = 1/2 l_{A-A}$$

$$r_B = 1/2 l_{B-B}$$

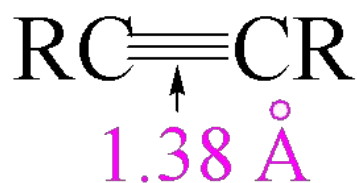
Аддитивная схема



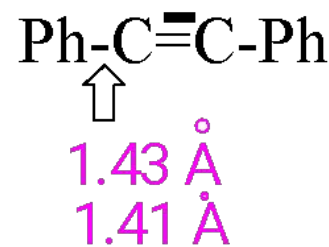
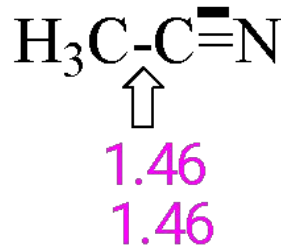
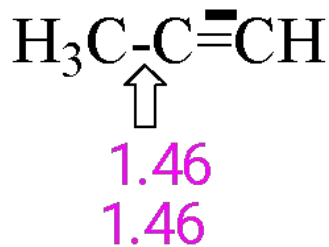
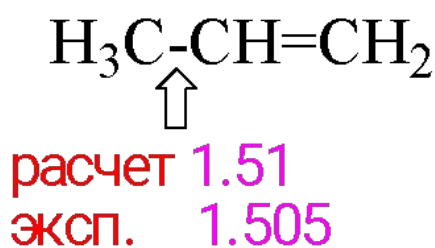
$$r_{\text{sp}^3}^{\text{C}} = 1.54/2 = 0.77 \text{ \AA}$$



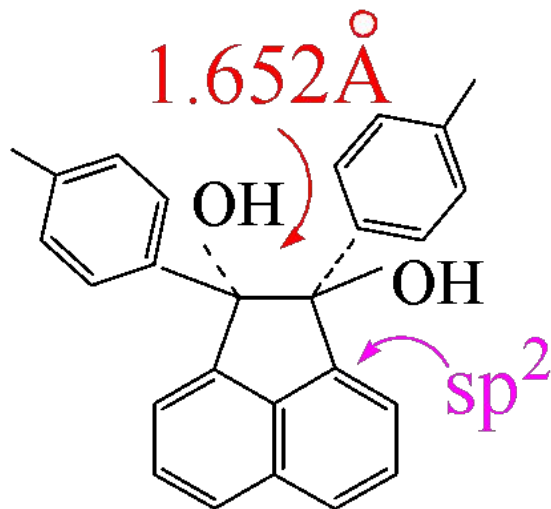
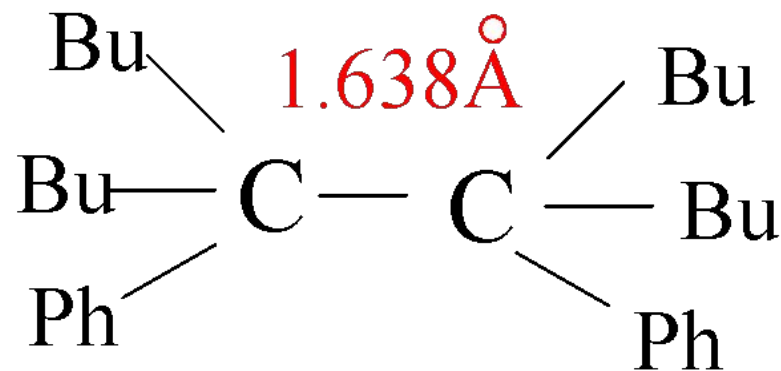
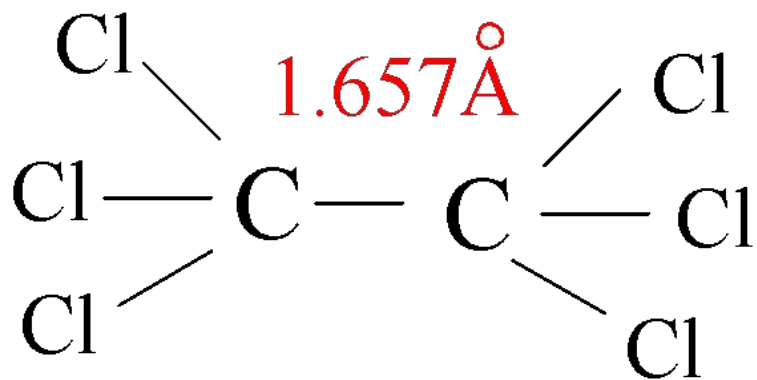
$$r_{\text{sp}^2}^{\text{C}} = 1.49/2 = 0.745 \text{ \AA}$$



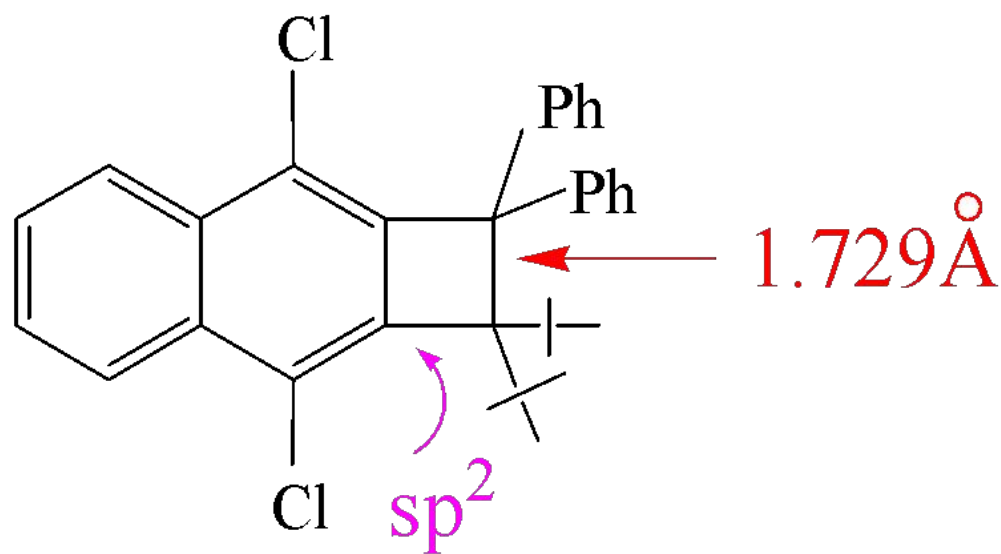
$$r_{\text{sp}}^{\text{C}} = 1.38/2 = 0.69 \text{ \AA}$$



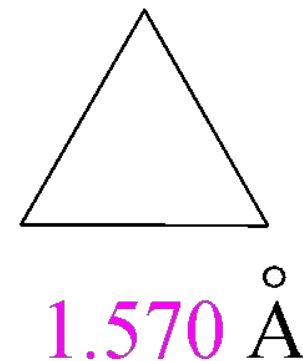
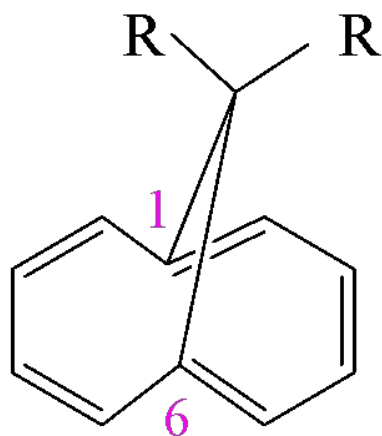
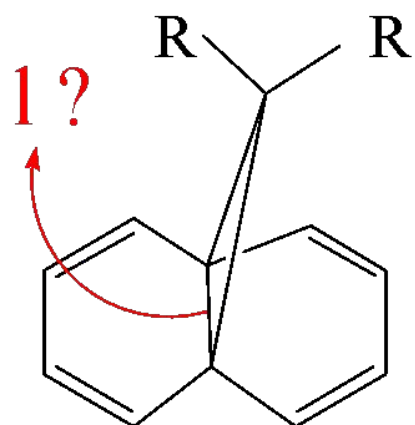
Необычно длинные связи



ЖСХ 1984, 142



J. Org. Chem., 1999, 3102



$$R = \text{CN} \quad l = 1.543 \text{ \AA}$$

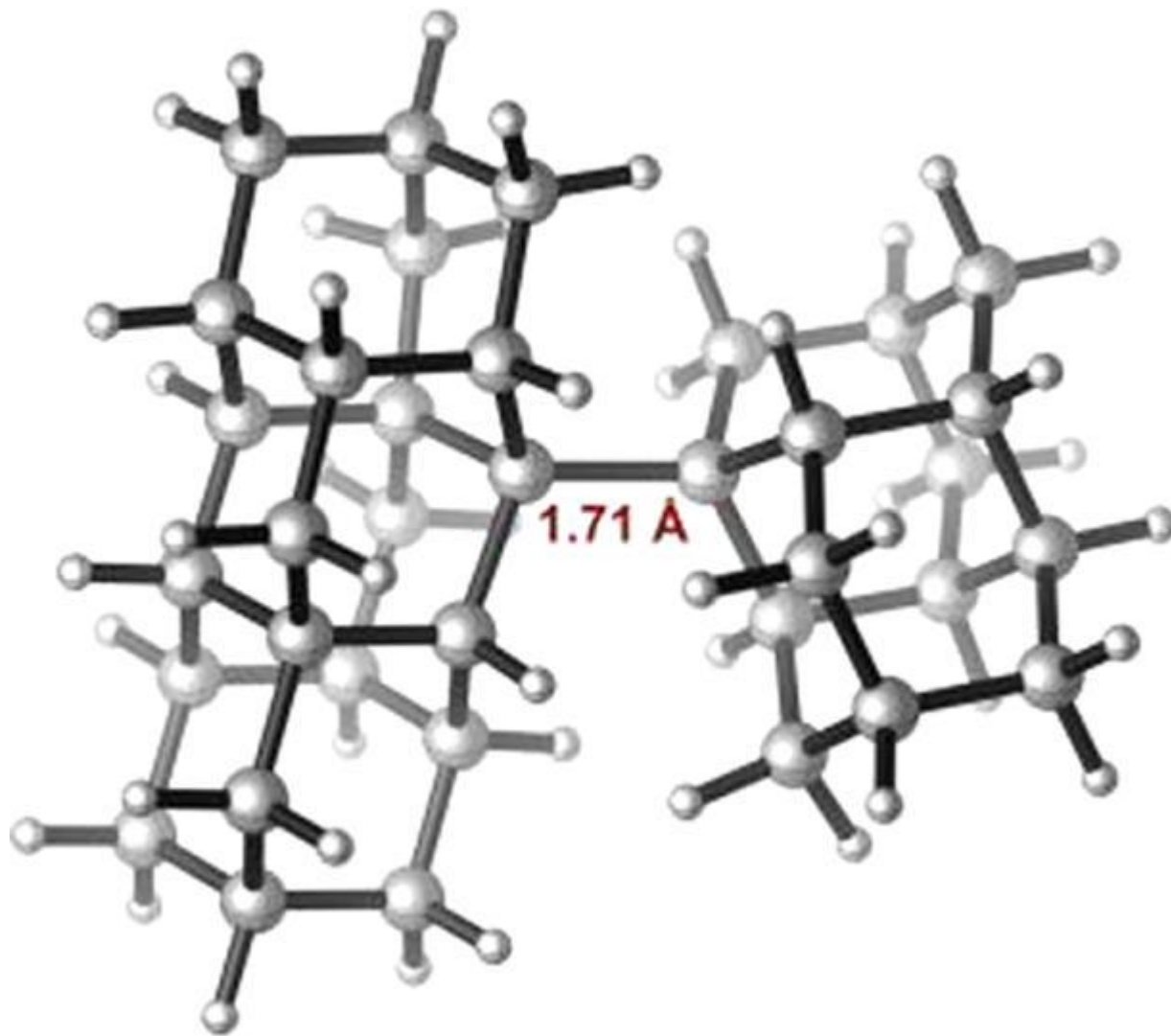
$$R = \text{Me} \quad l = 1.770 \text{ \AA} \quad \text{lim}$$

$$R = \text{F} \quad l = 2.269 \text{ \AA}$$

Высокая эллиптичность
связи C¹-C⁶

Атомы в молекулах. Р. Бейдер. 2001.

2-(1-diamantyl)[121]tetramantane



J. Am. Chem. Soc. 2012, 13641

Энергия «искажения»

Удлинение связи:

$$E_1 = \sum k_1 (\Delta l)^2$$

Деформация углов:

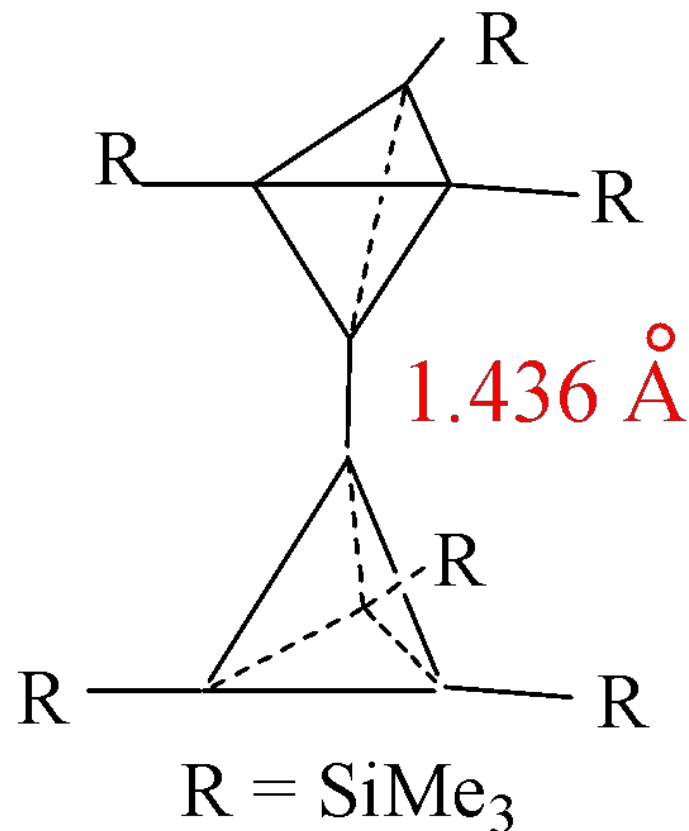
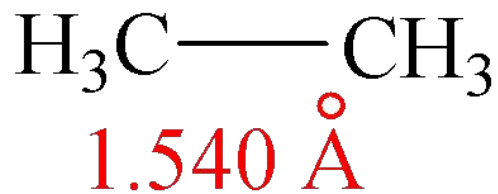
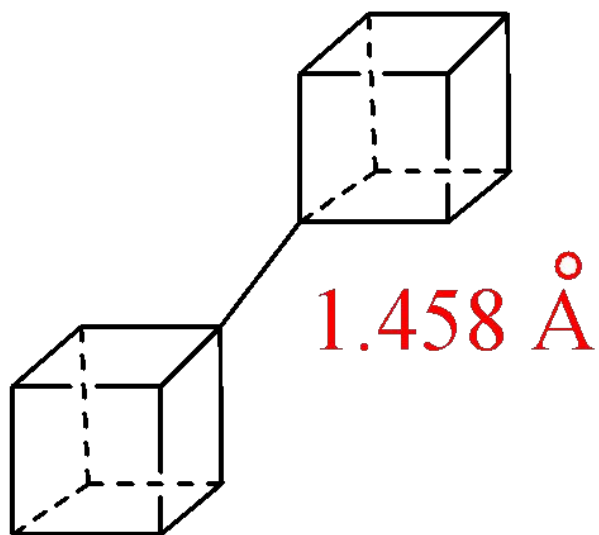
$$E_\varphi = \sum k_\varphi / 2 (\Delta\varphi)^2$$

Ван-дер-ваальсовы радиусы

N 1.50	O 1.40	F 1.35
P 1.90	S 1.85	Cl 1.80
As 2.00	Se 2.00	Br 1.95
H 1.10	C 1.70	I 2.15

Л. Полинг, П. Полинг. Химия. М.: Мир, 1978; R. S. Rowland and R. Taylor, J. Phys. Chem., 100, 7384(1996); A. Bondi, J. Phys. Chem., 68, 441 (1964)

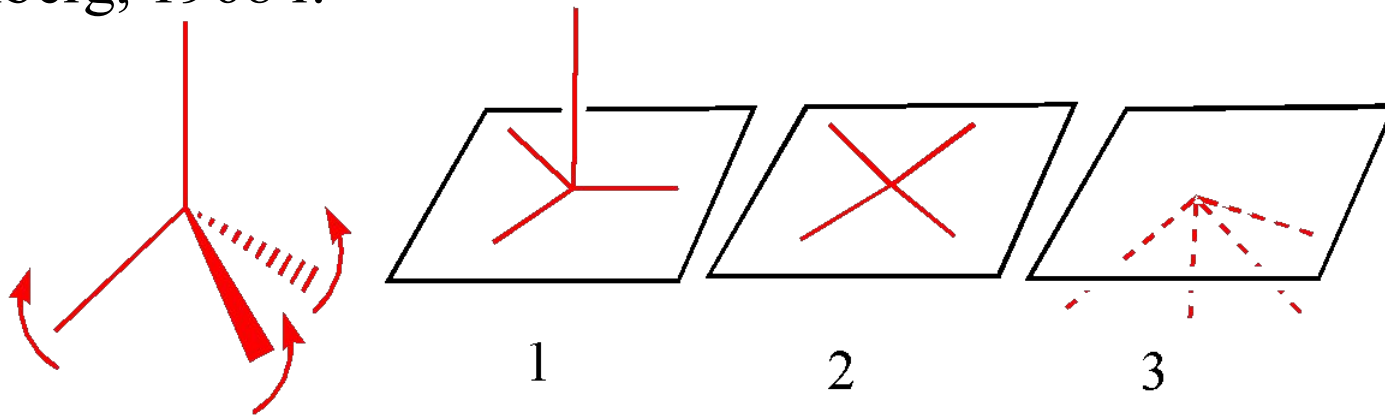
«Сжатие» С-С связи



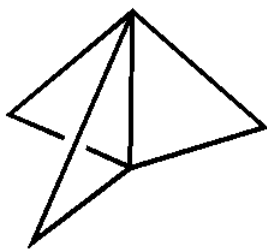
Ang. Chem. Int., 2005, 5821

Соединения с инвертированной тетрагональной геометрией

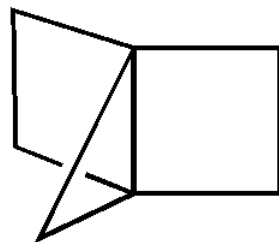
К. Wiberg, 1968 г.



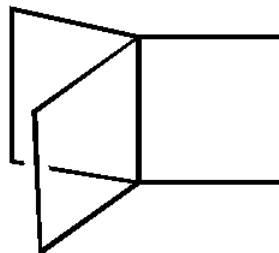
Пропелланы



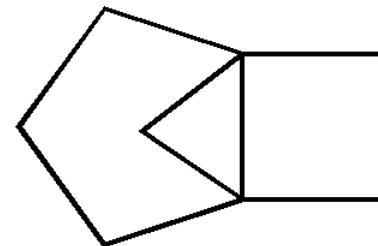
1,1,1-



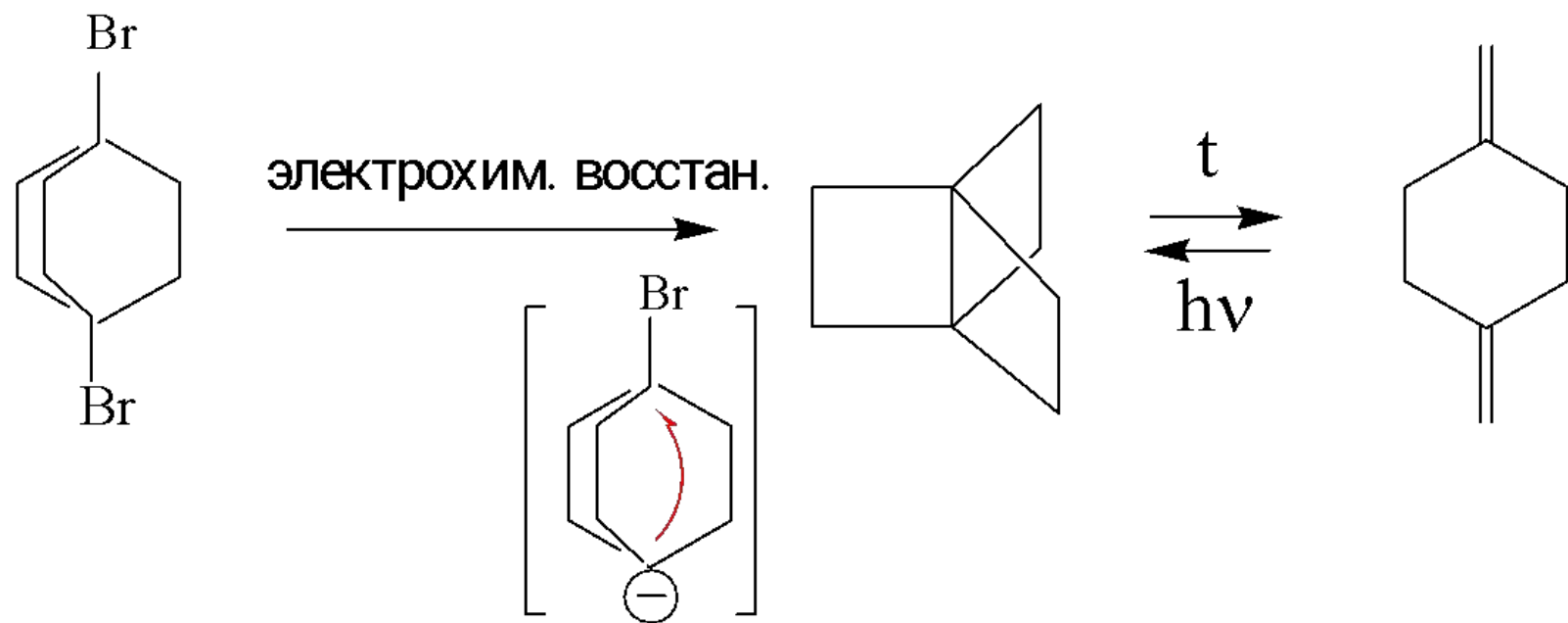
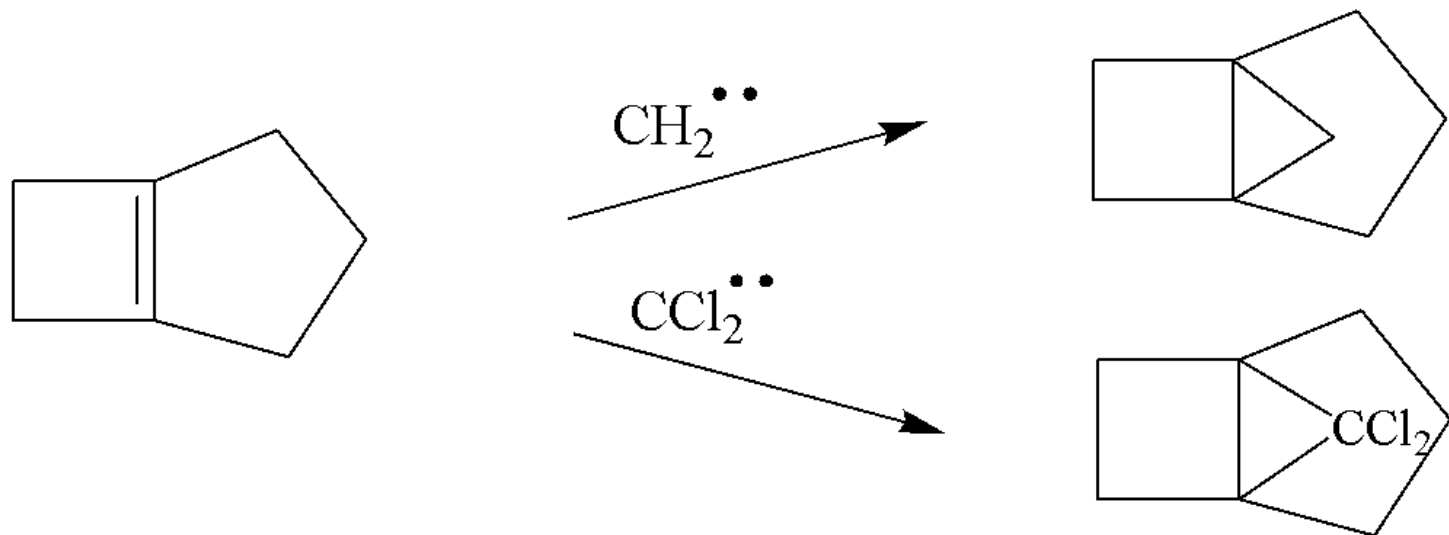
1,2,2-

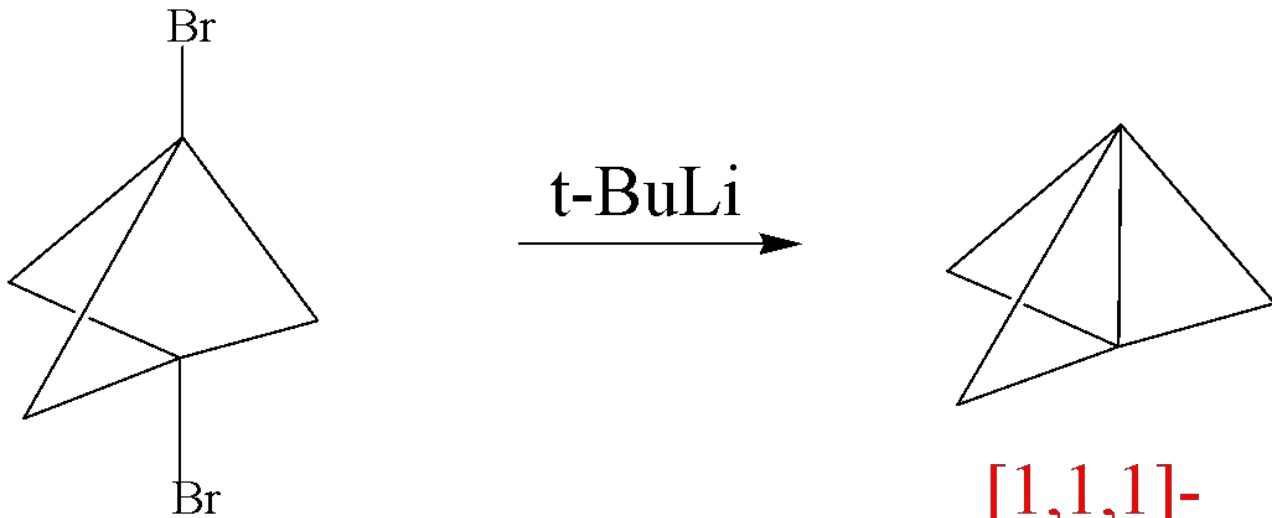


2,2,2-

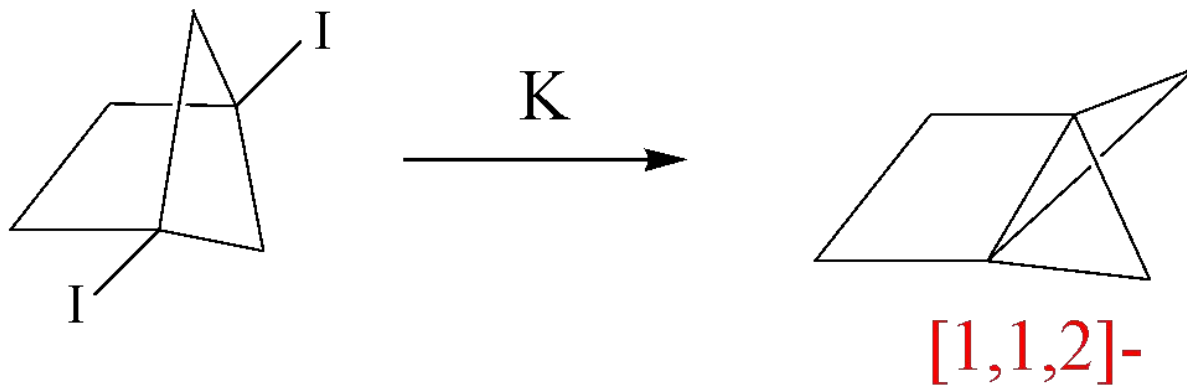


1,2,3-



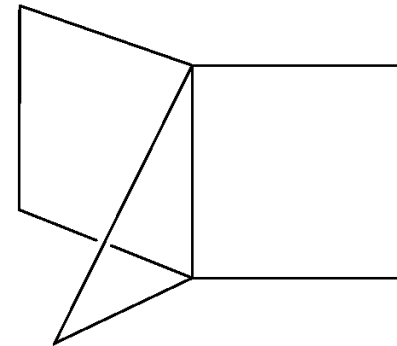
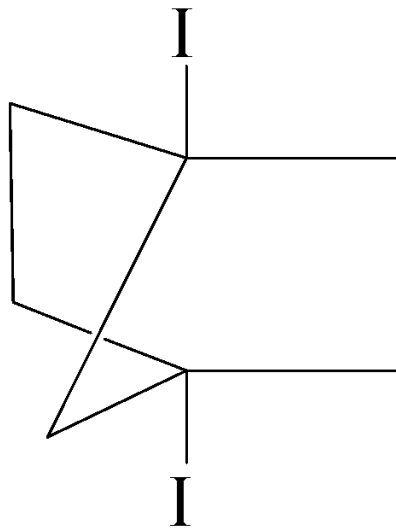


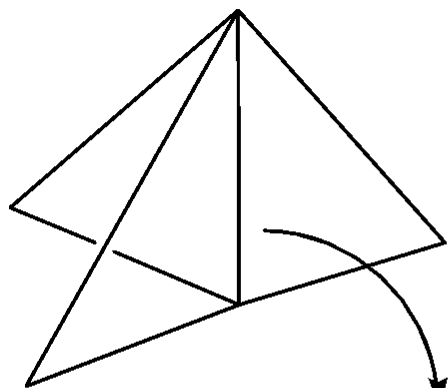
[1,1,1]-
 ЯМР ^1H : δ , м.д., 2.06 ЯМР ^{13}C : δ , м.д., 1.0 (C),
 74.2 (CH_2)



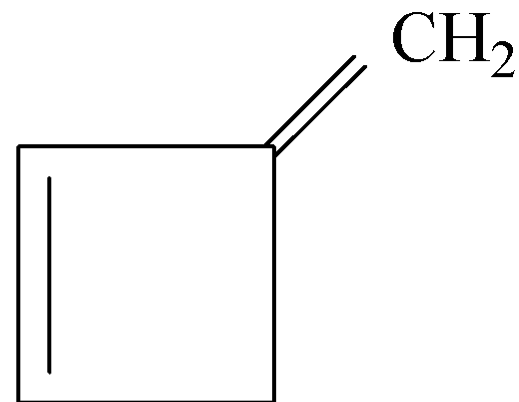
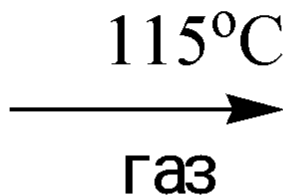
[1,1,2]-

K. Wiberg et al., JACS **1982**, 5239; **1983**, 3635

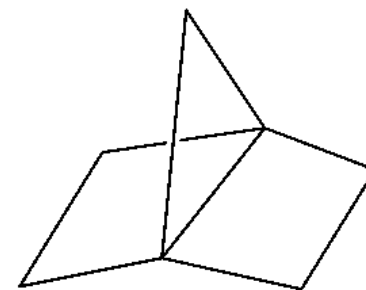
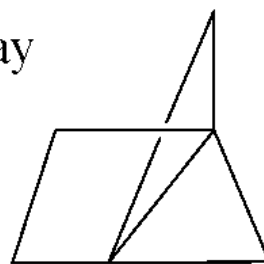
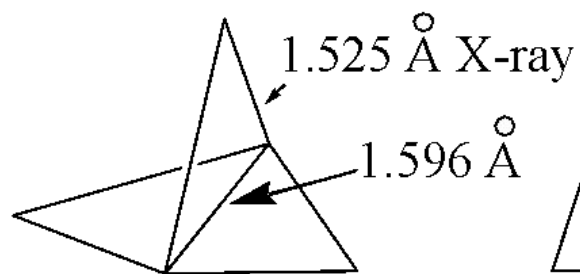




1.543 Å
ab initio



Энергия напряжения SE



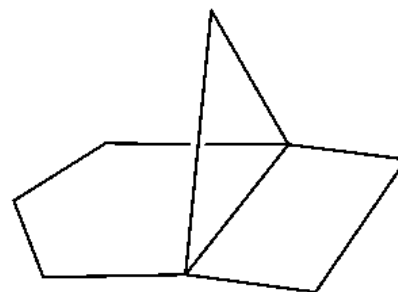
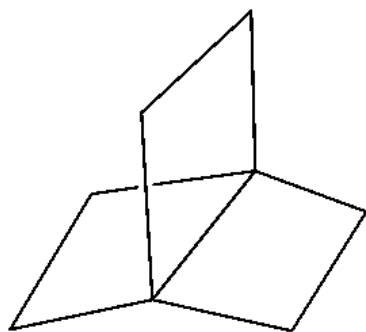
SE,

102

104

102

ккал/моль



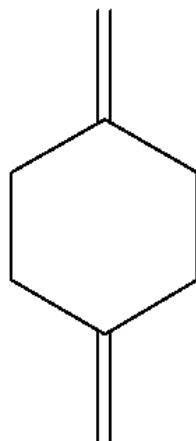
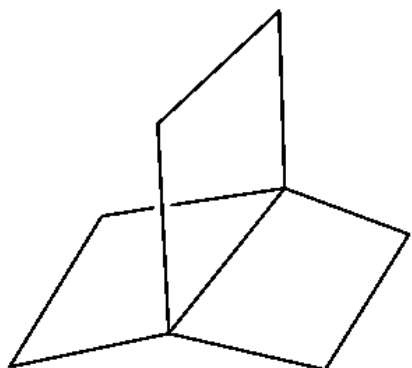
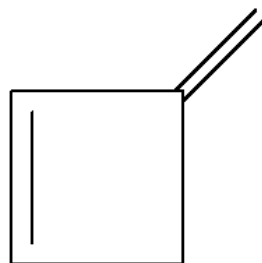
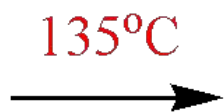
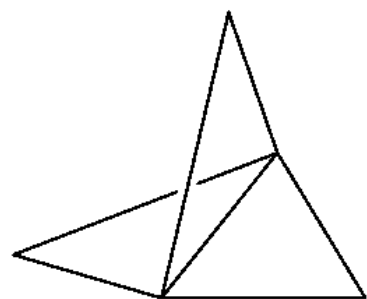
SE,

93

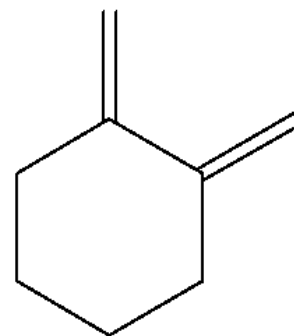
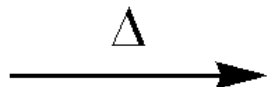
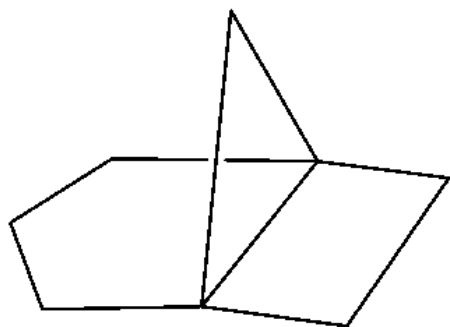
67

ab initio 6-31G

ккал/моль

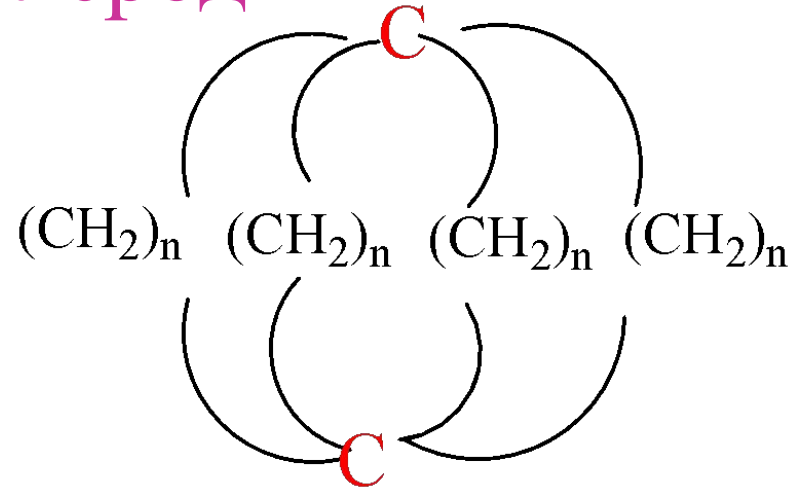
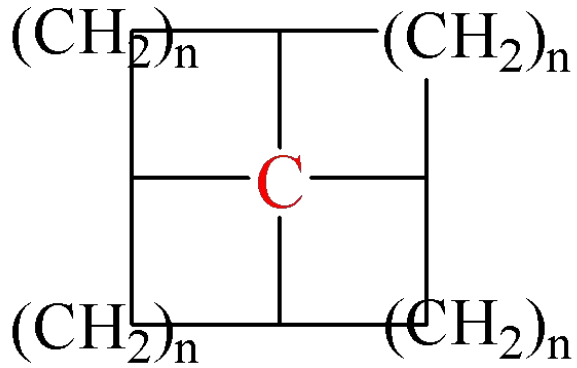


$t_{1/2}$ 1 час, 20°C



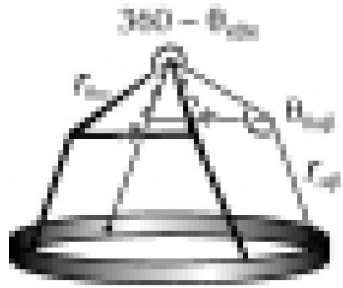
$t_{1/2}$ 1 час, 320°C

Планарный углерод

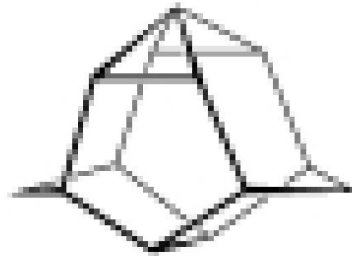


фенестраны

пэддланы



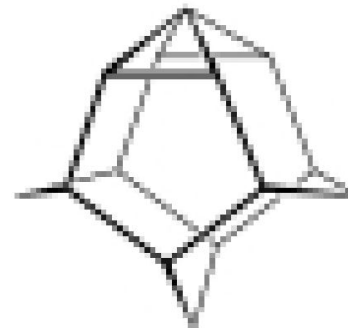
IV



5

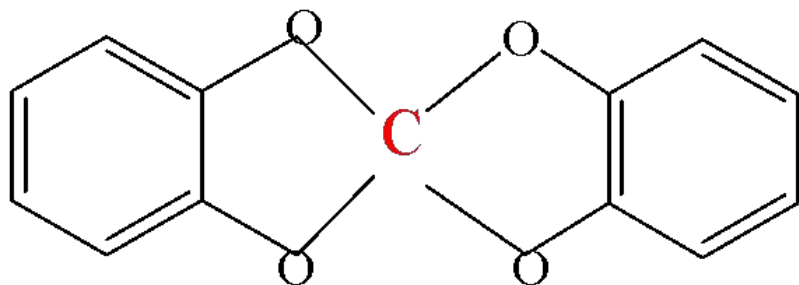


6

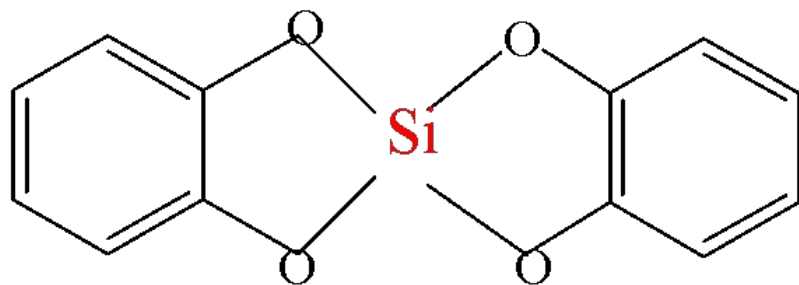


7

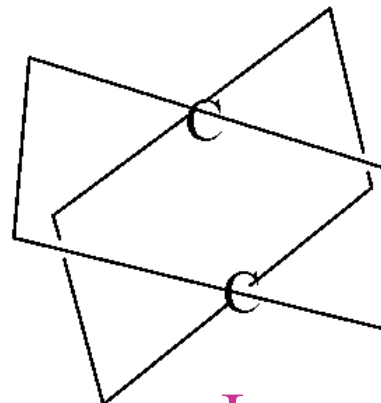
В кристалле



II (тетраэдр)



III (планарен)

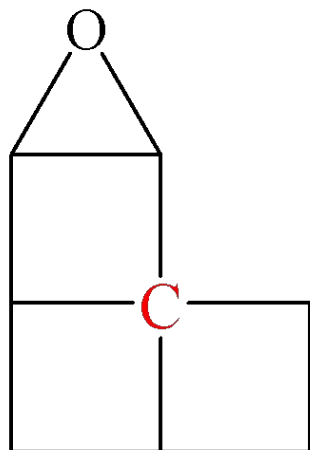


I

ab initio (STO-3G)
 $\Delta\Delta E$, ккал/моль

CH₄ 240

SiH₄ 152

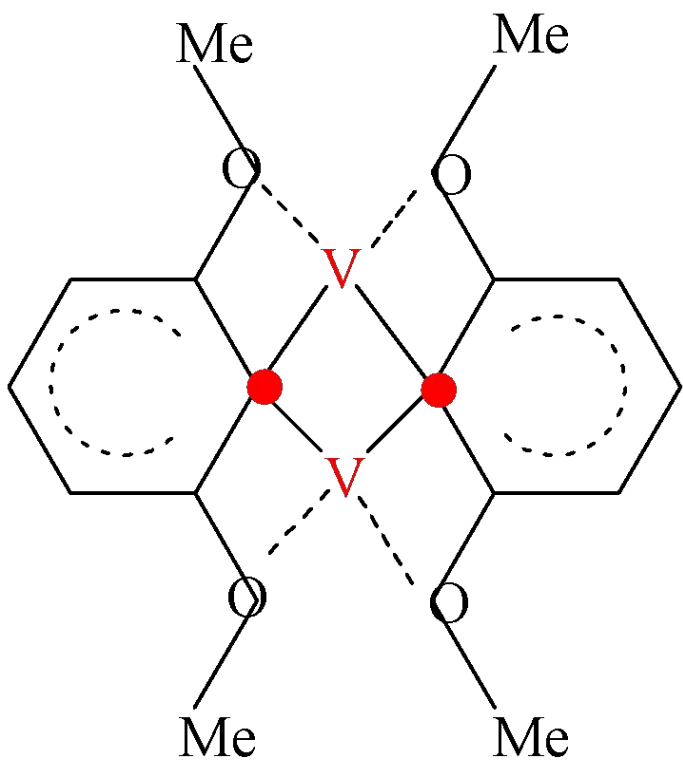


strasбурген

Редакция J. Chem. Res. (1977 г.)

«Первый синтез производного
планарного тетракоординированного С»

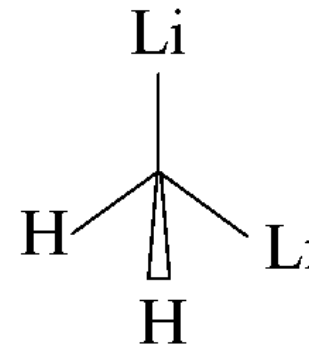
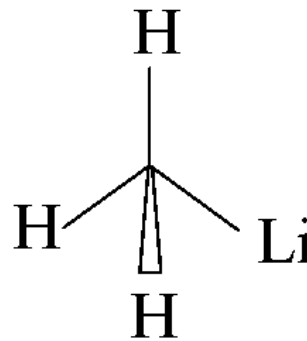
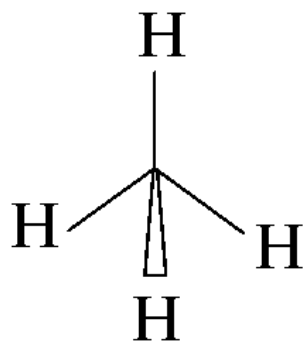
Рислинг, 1977 г.



Cotton, Millar, JACS, 1977

«Планаризация» соединений углерода

ab initio



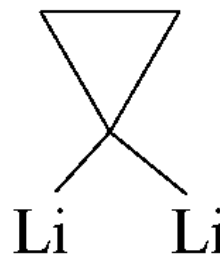
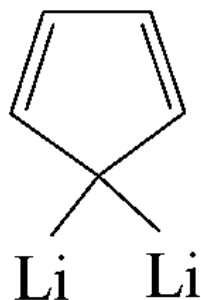
$\Delta\Delta E,$

122

52

17

ккал/ моль



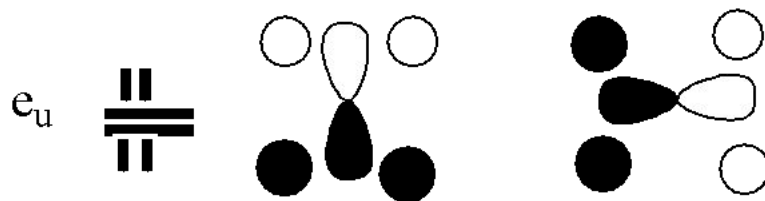
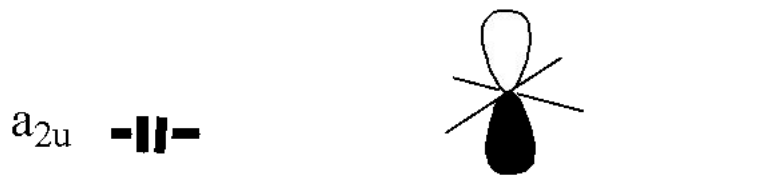
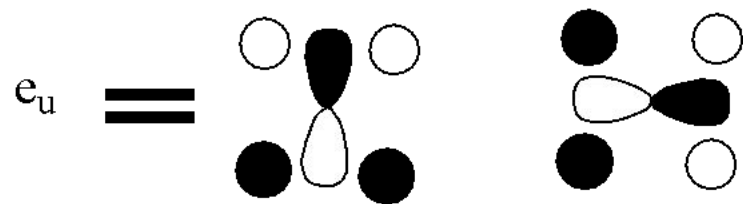
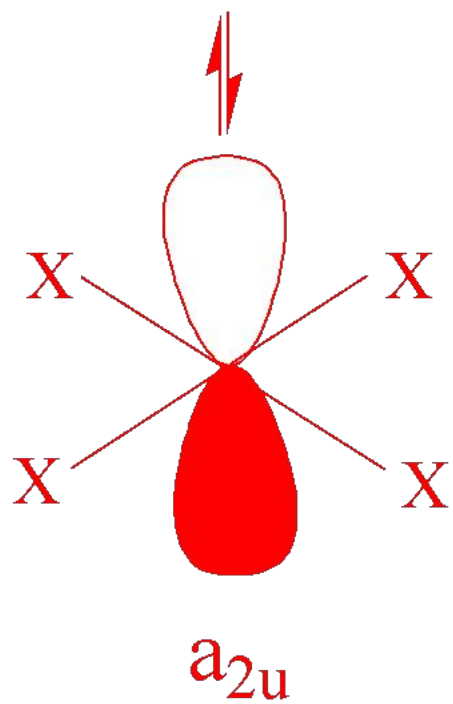
$\Delta\Delta E,$

16

-7

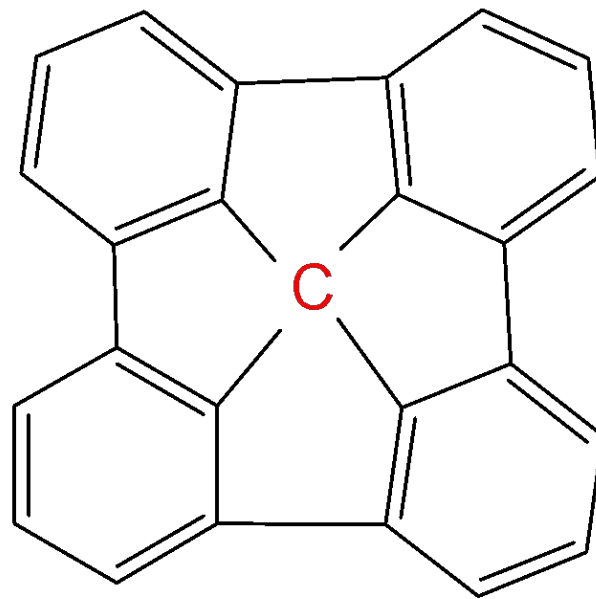
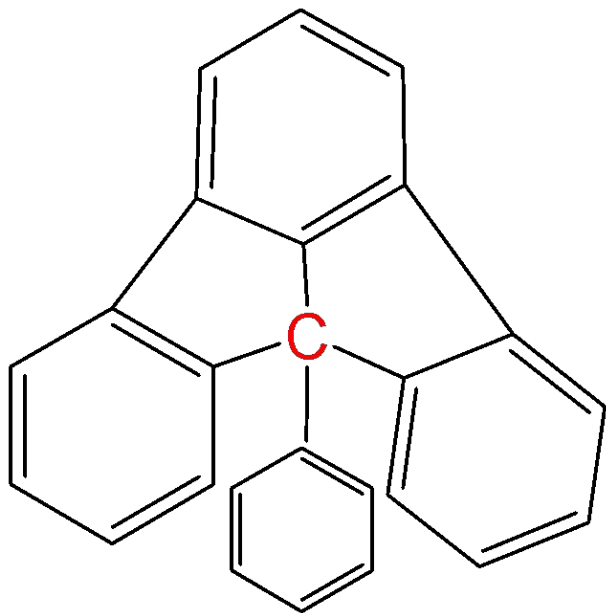
ккал/ моль

P. Schleyer et al. Ang. Chem. Int., 1997, 815



Fluradenes

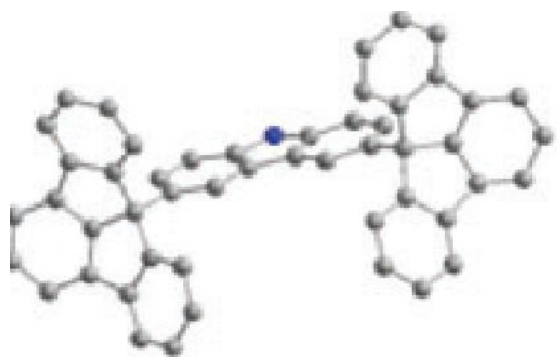
Q. Liu et al., Chem. Comm. **2011**, 2155



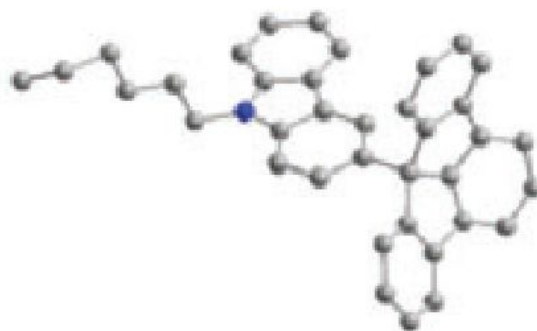
Не синтезированы

Fluradenes

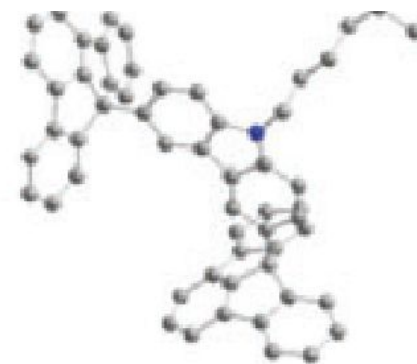
Q. Liu et al., Chem. Comm. 2011, 2155



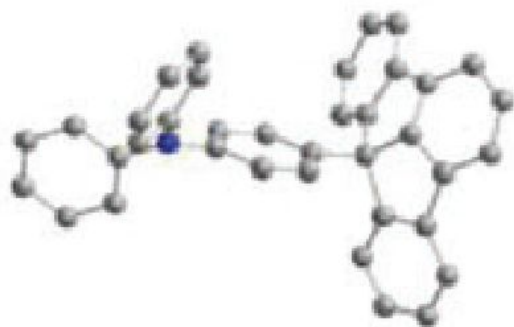
4a



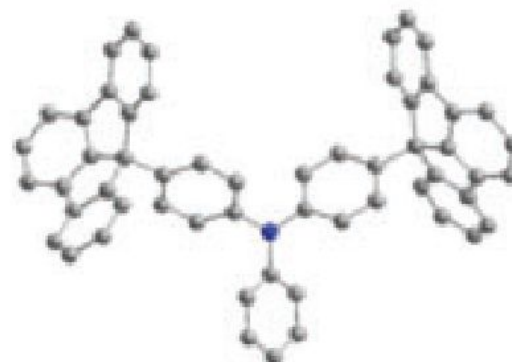
4ba



4bb



4ca



4cb