Теоретические основы органической химии

Соединения с инвертированной геометрией

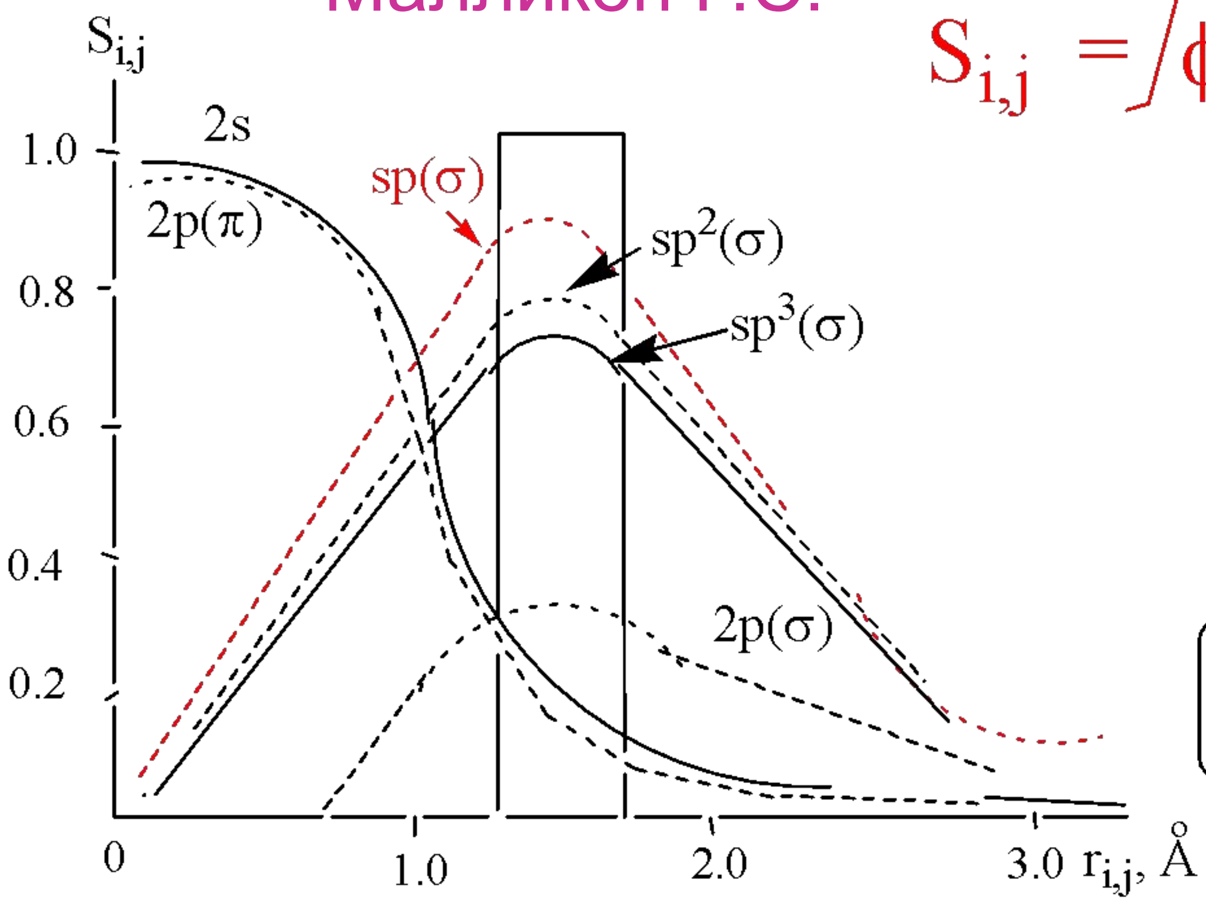
Лекция 4
(мультимедийный курс)

Проф. Бородкин Г.И.

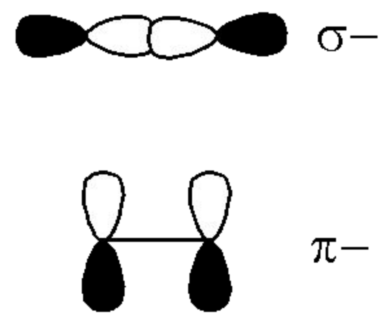
Теория гибридизации

1. Направленность орбиталей
2. Принцип максимального орбитального перекрывания

Малликен Р.С.



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



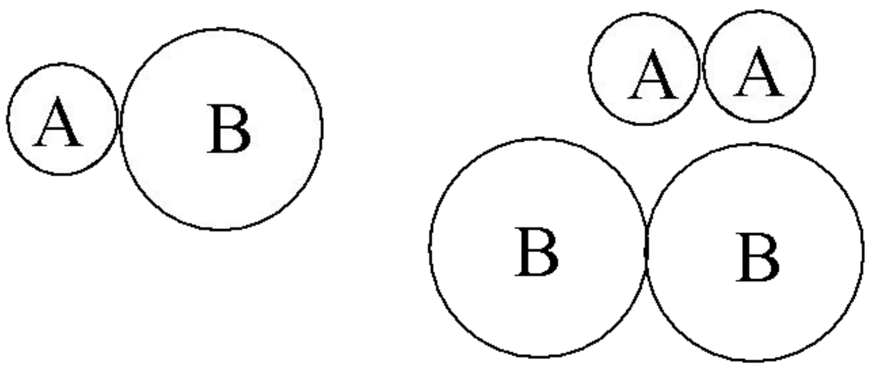
$sp^3 < sp^2 < sp$

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≡CH	sp	114	1.061

ПМП !

прочность связи ↓ укороче-ние ↓

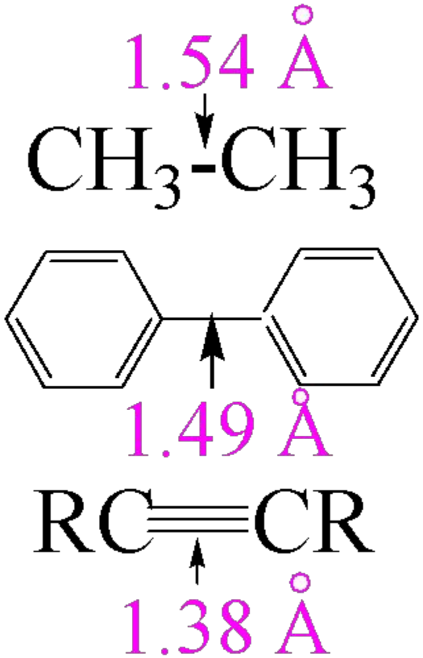
Ковалентный радиус



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

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

Аддитивная схема



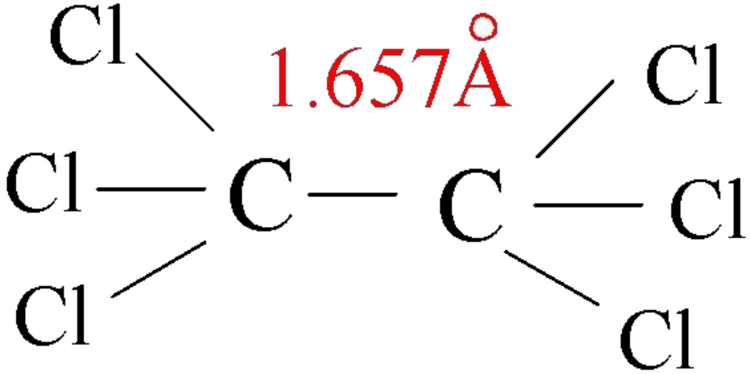
$$r^{C}_{sp^3} = 1.54/2 = 0.77\ \text{Å}$$

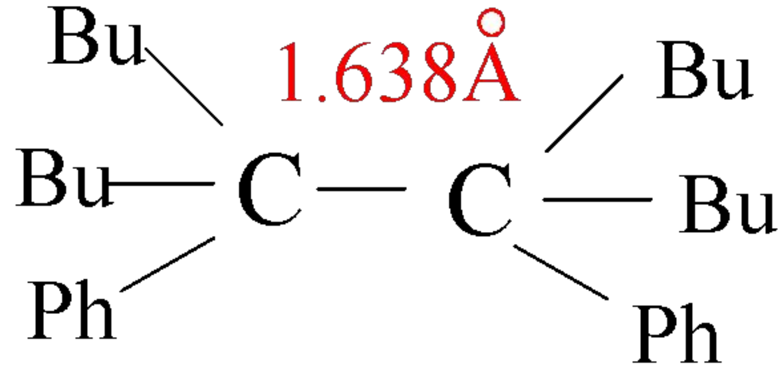
$$r^{C}_{sp^2} = 1.49/2 = 0.745\ \text{Å}$$

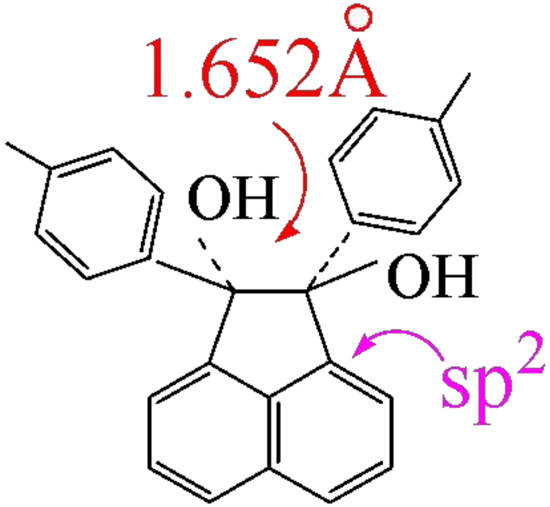
$$r^{C}_{sp} = 1.38/2 = 0.69\ \text{Å}$$

	H_3C-CH=CH_2	H_3C-C≡CH	H_3C-C≡N	Ph-C≡C-Ph
расчет	1.51	1.46	1.46	1.43 Å
эксп.	1.505	1.46	1.46	1.41 Å

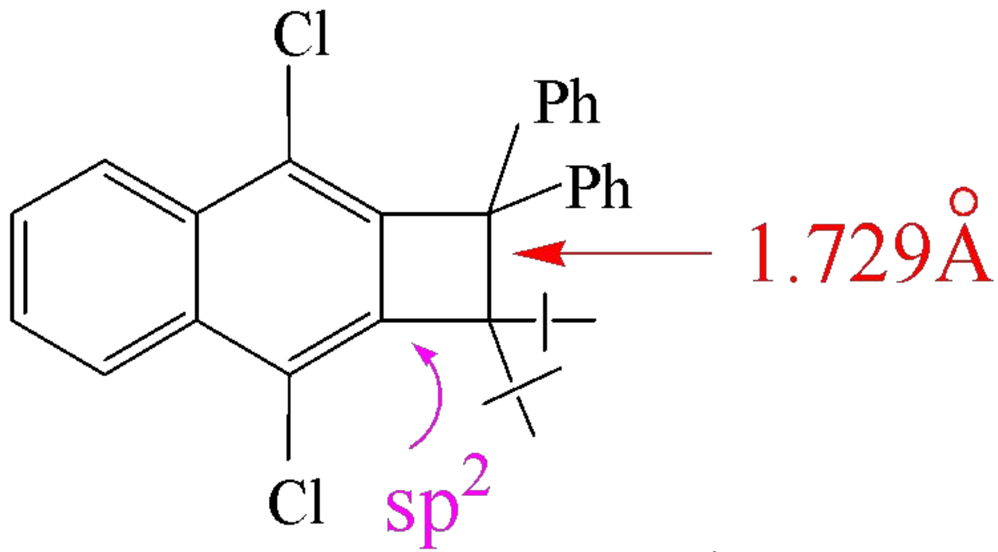
Необычно длинные связи



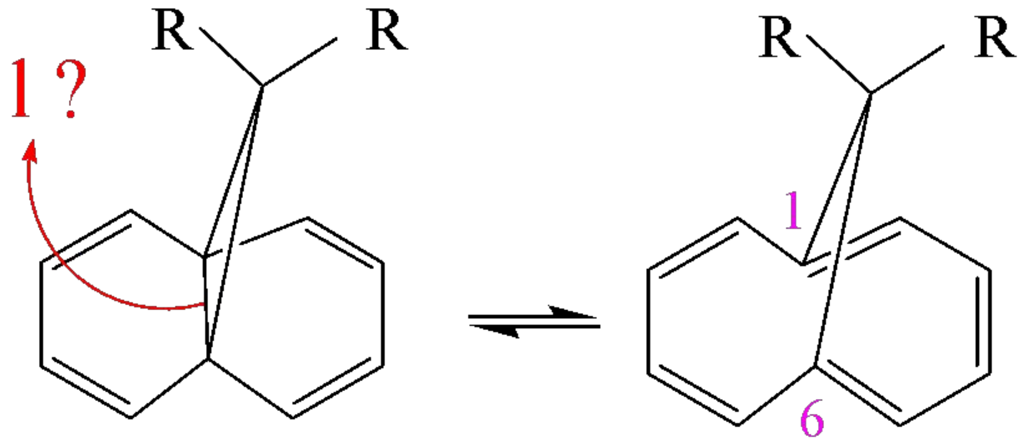


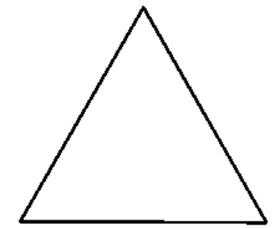


ЖСХ **1984**, 142



J. Org. Chem., **1999**, 3102





1.570 Å

R = CN l = 1.543 Å

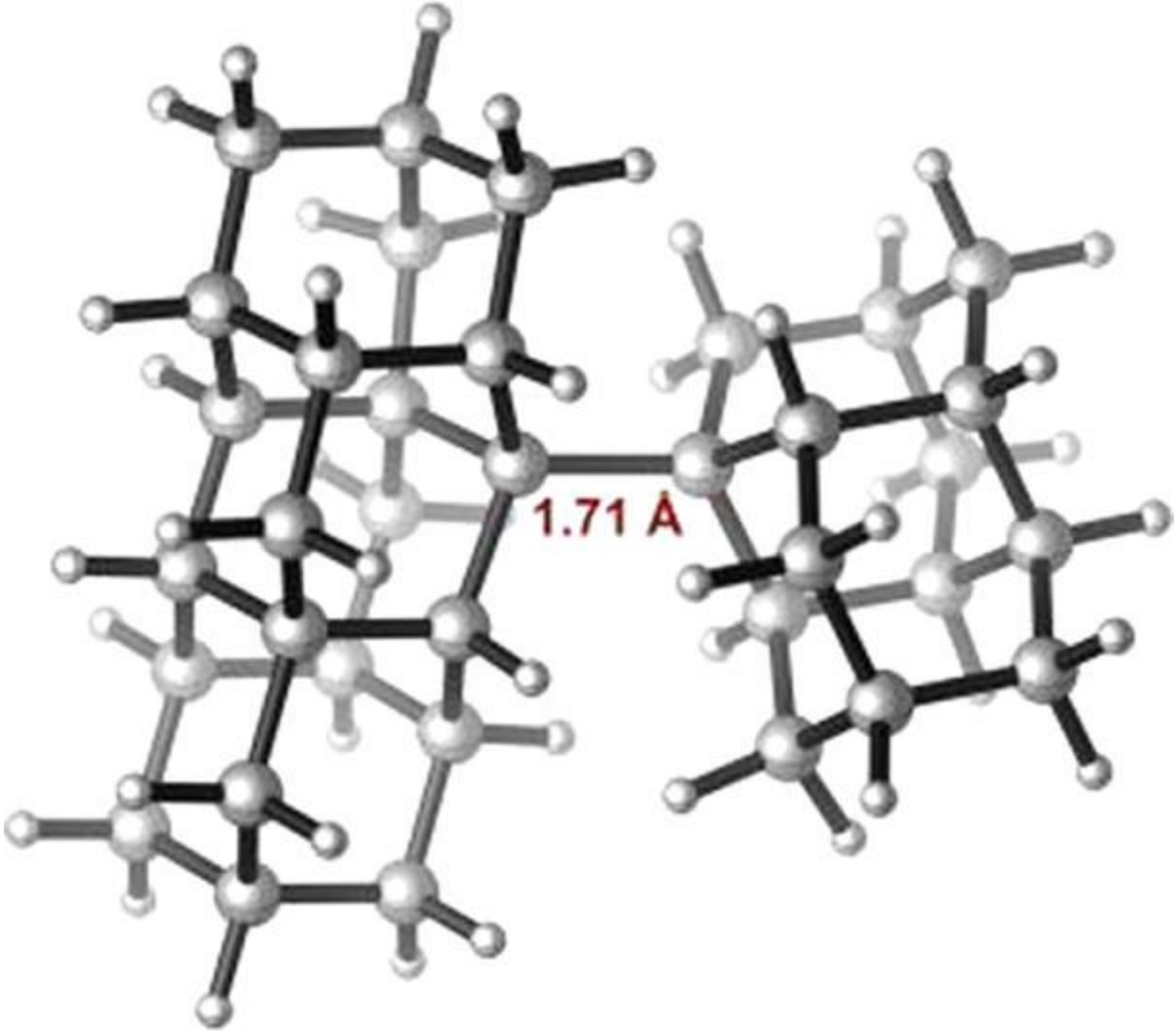
R = Me l = 1.770 Å lim

R = F l = 2.269 Å

Высокая эллиптичность связи C^1-C^6

Атомы в молекулах. Р. Бейдер. 2001.

2-(1-diamantyl)[121]tetramantane



J. Am. Chem. Soc. 2012, 13641

Энергия «искажения»

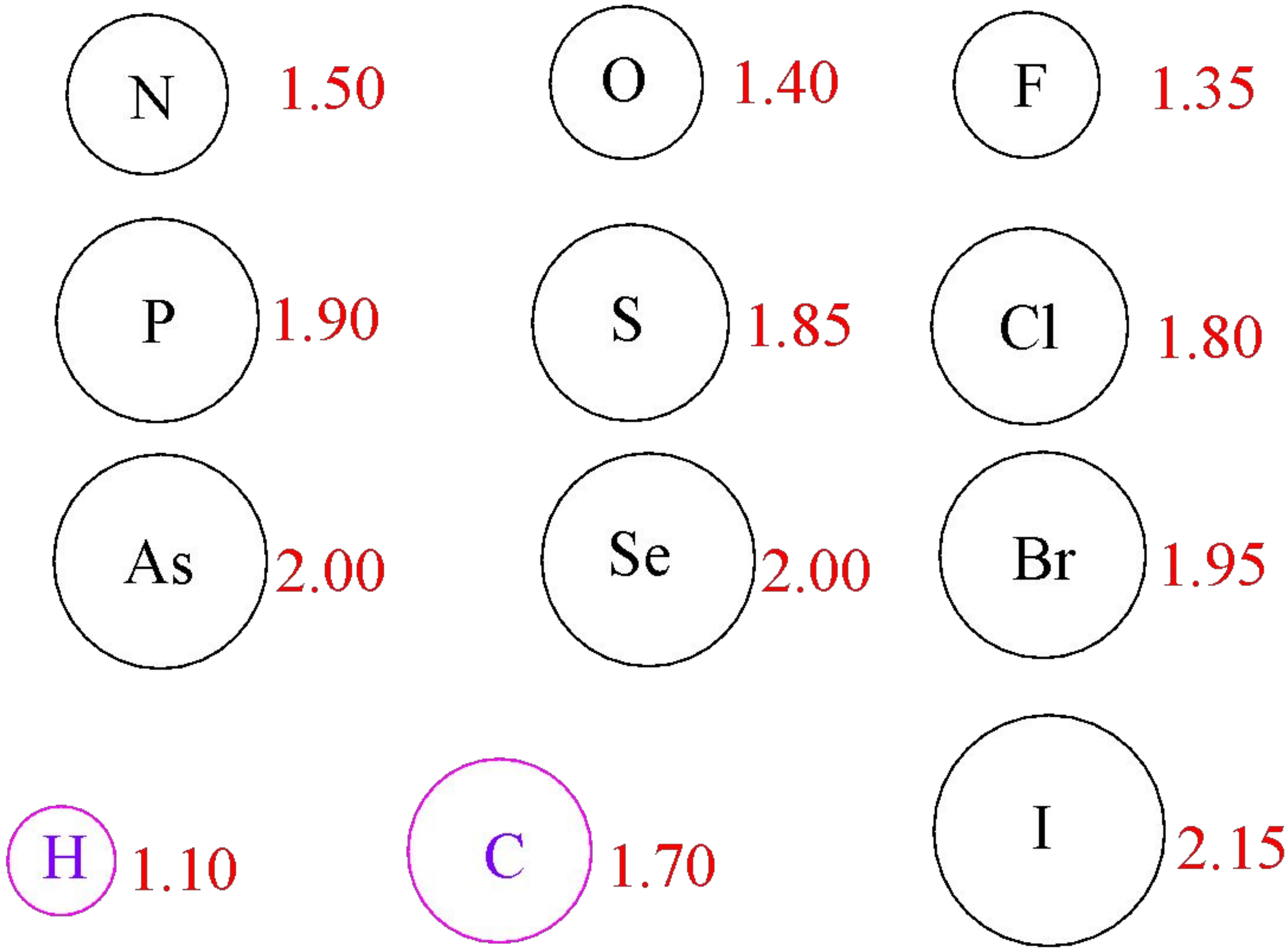
Удлинение связи:

$$E_l = \Sigma k_l (\Delta l)^2$$

Деформация углов:

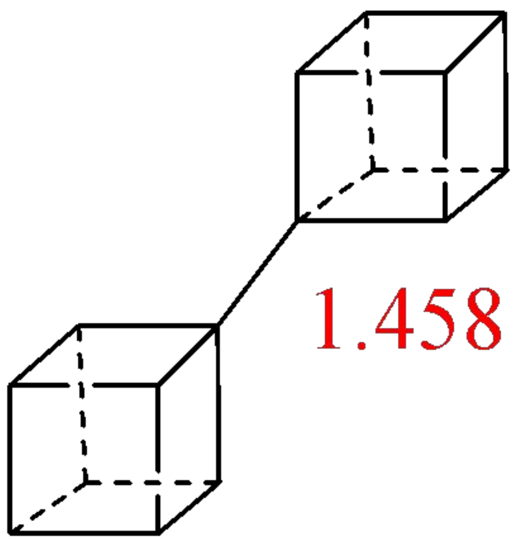
$$E_\varphi = \Sigma k_\varphi /2 (\Delta\varphi)^2$$

Ван-дер-ваальсовсы радиусы



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)

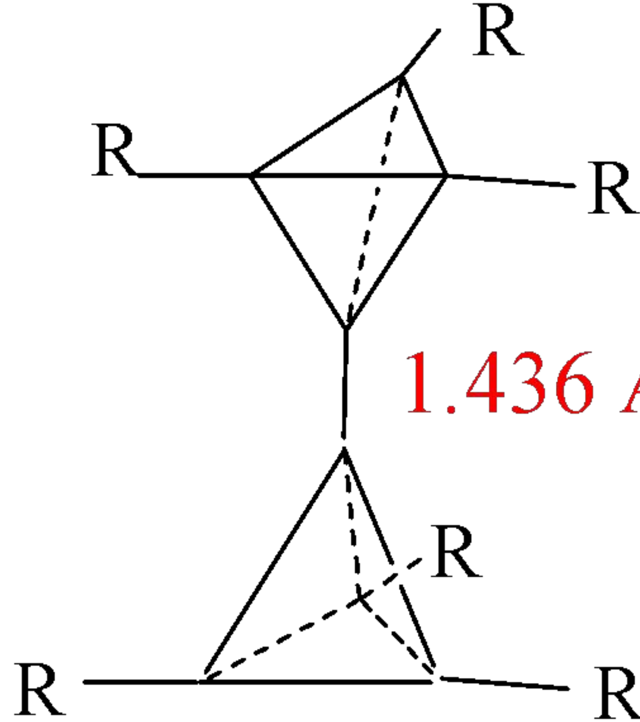
«Сжатие» С-С связи



1.458 Å

$H_3C—CH_3$

1.540 Å



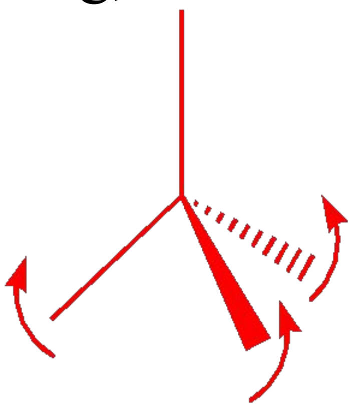
1.436 Å

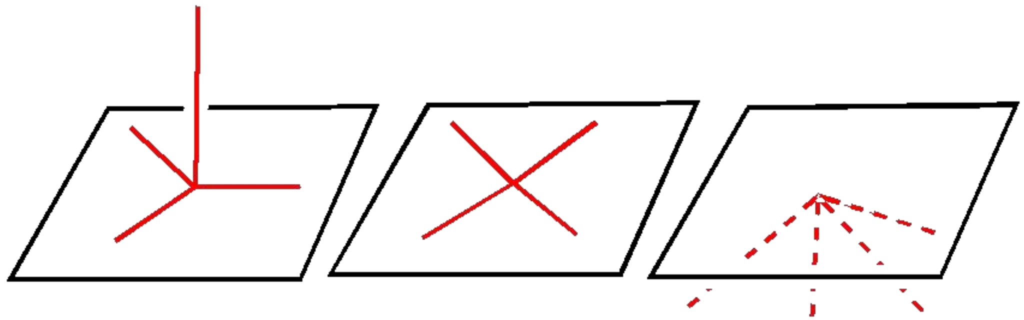
R = $SiMe_3$

Ang. Chem. Int., **2005**, 5821

Соединения с инвертированной тетрагональной геометрией

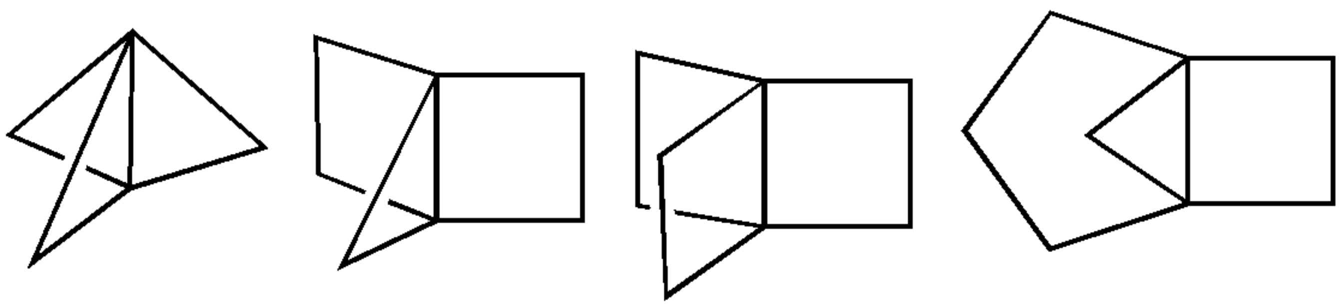
K. Wiberg, 1968 г.



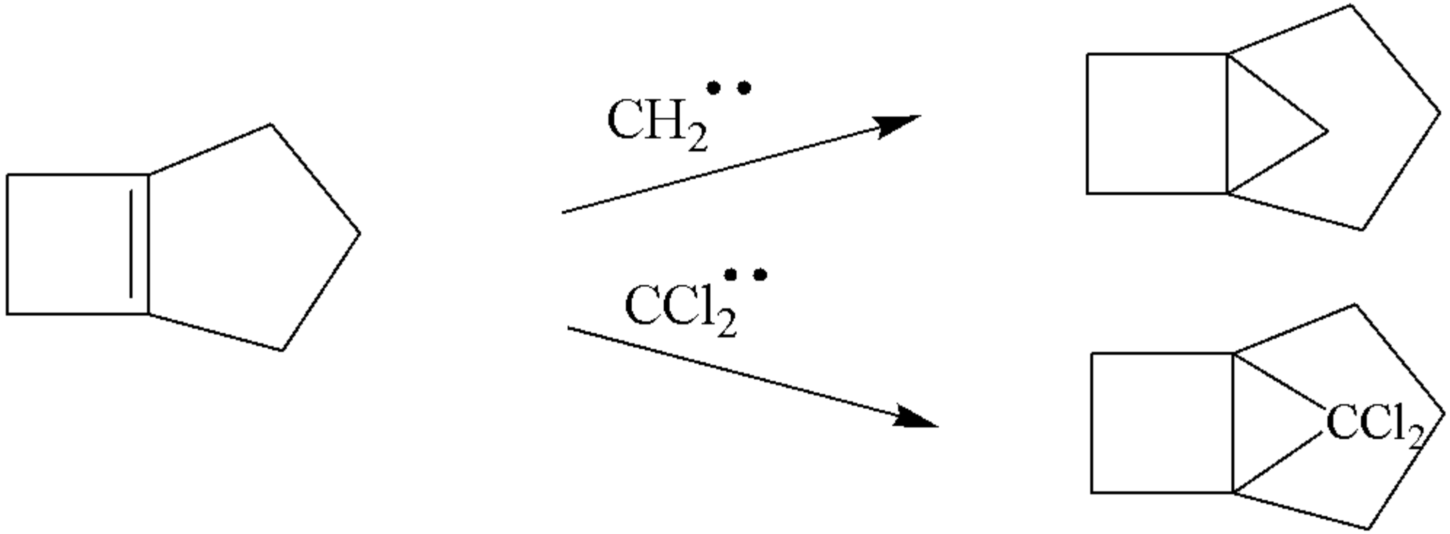


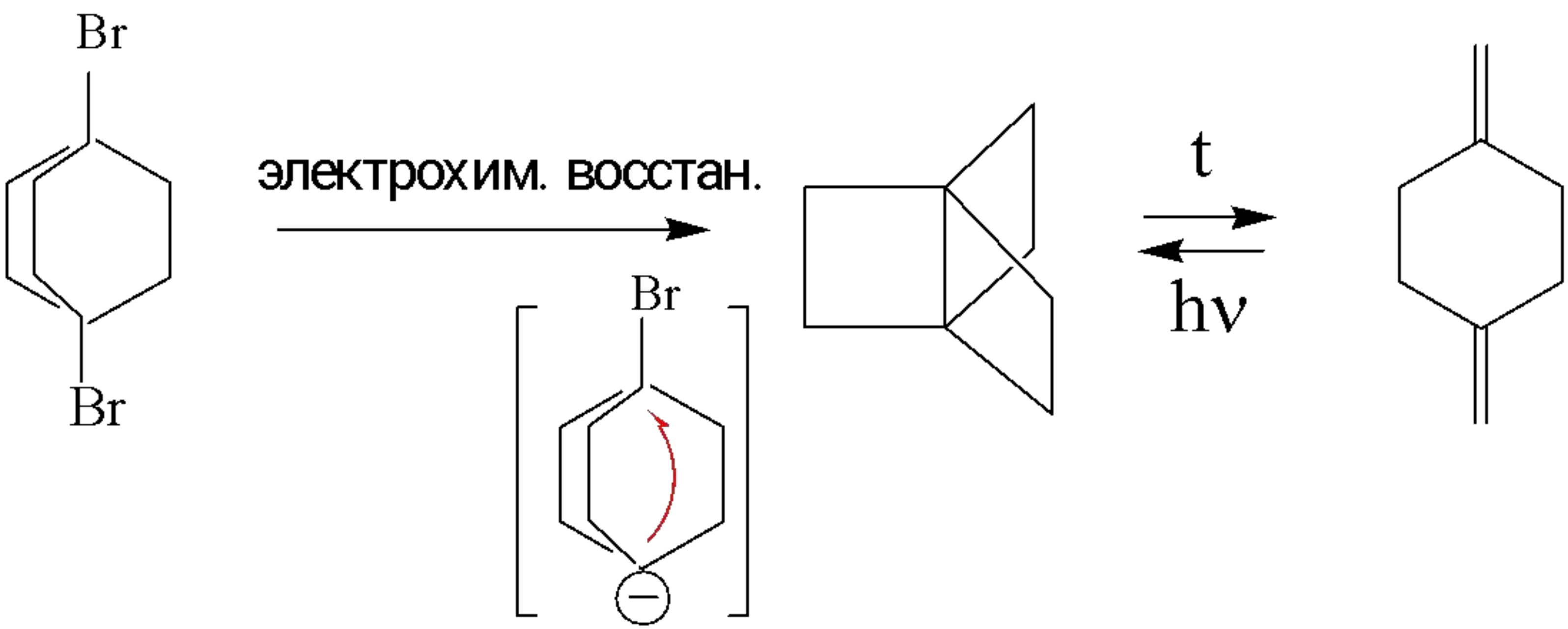
1 2 3

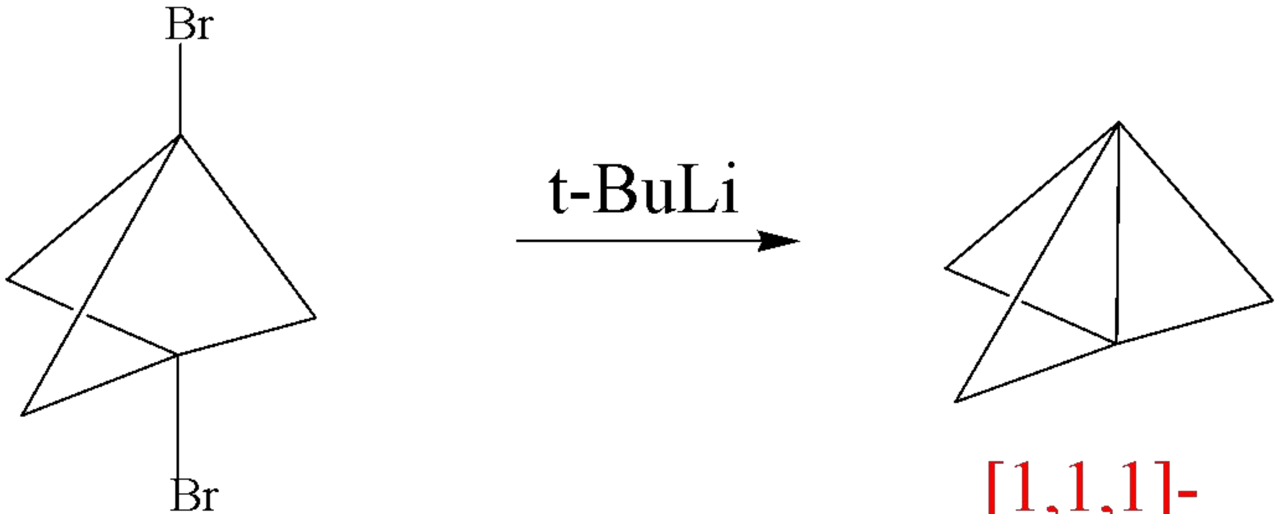
Пропелланы



1,1,1- 1,2,2- 2,2,2- 1,2,3-

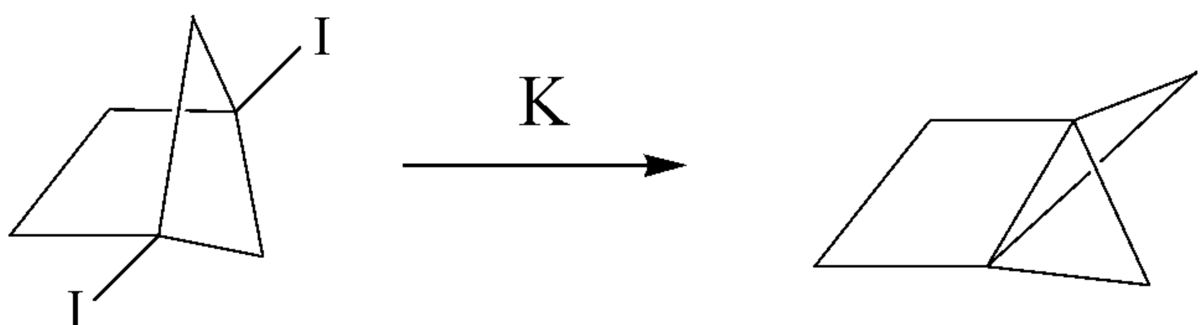

CH2
CCl2
CCl2


Br
Br
электрохим. восстан.
Br
t
hν



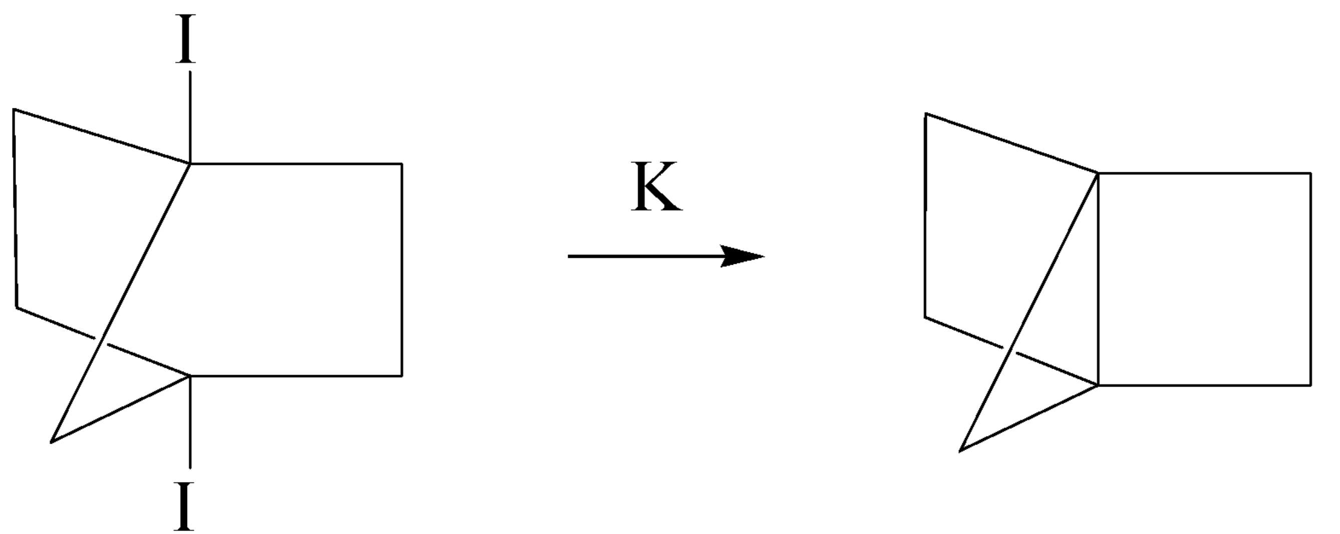
[1,1,1]-

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

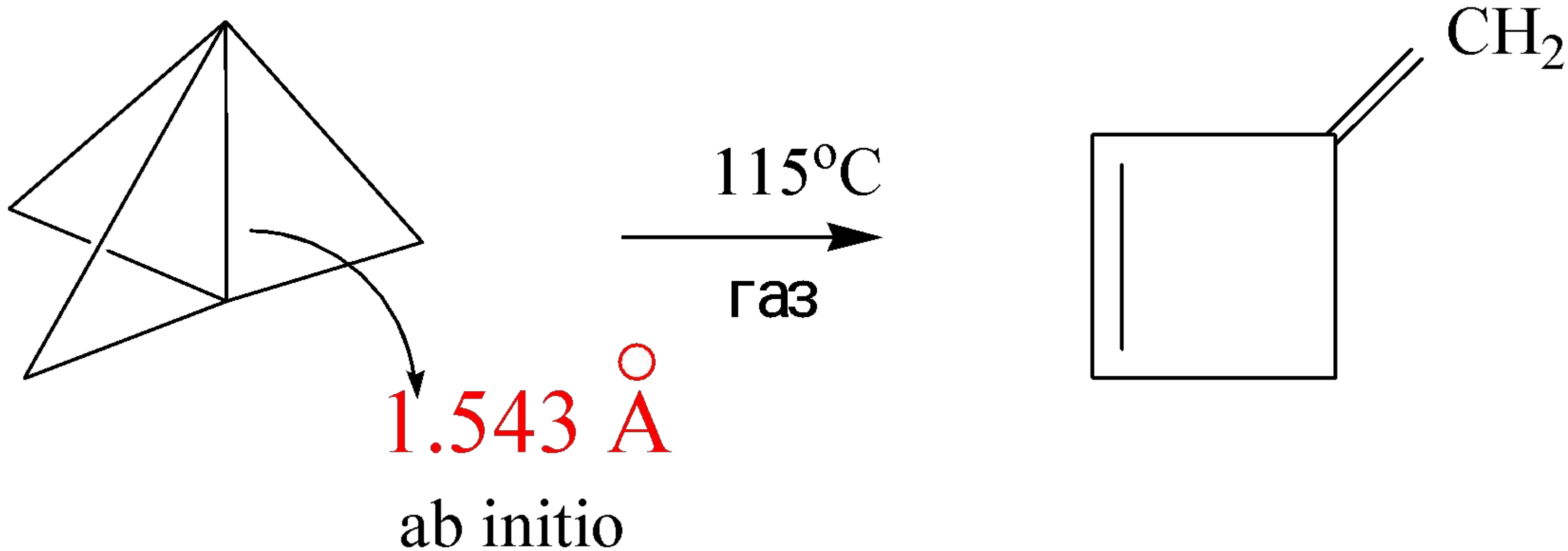


[1,1,2]-

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

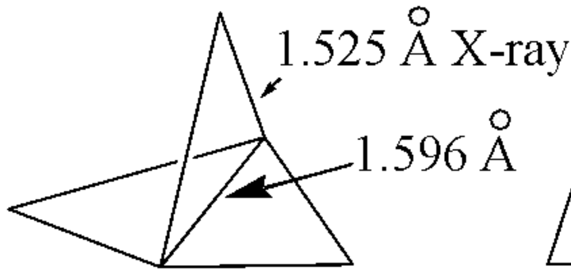


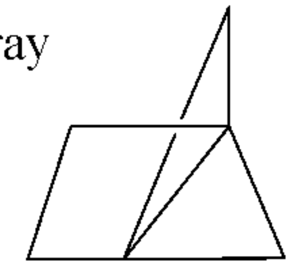
I
K
I

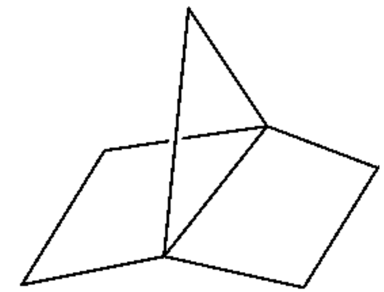


115°C
газ
1.543 Å
ab initio
CH2

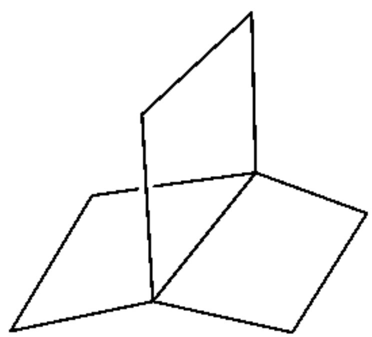
Энергия напряжения SE

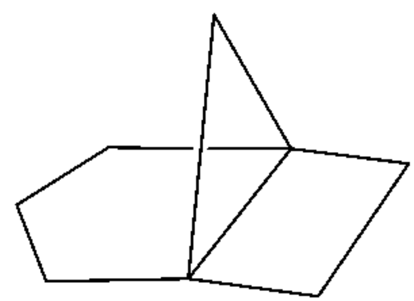






SE, ккал/моль: 102, 104, 102

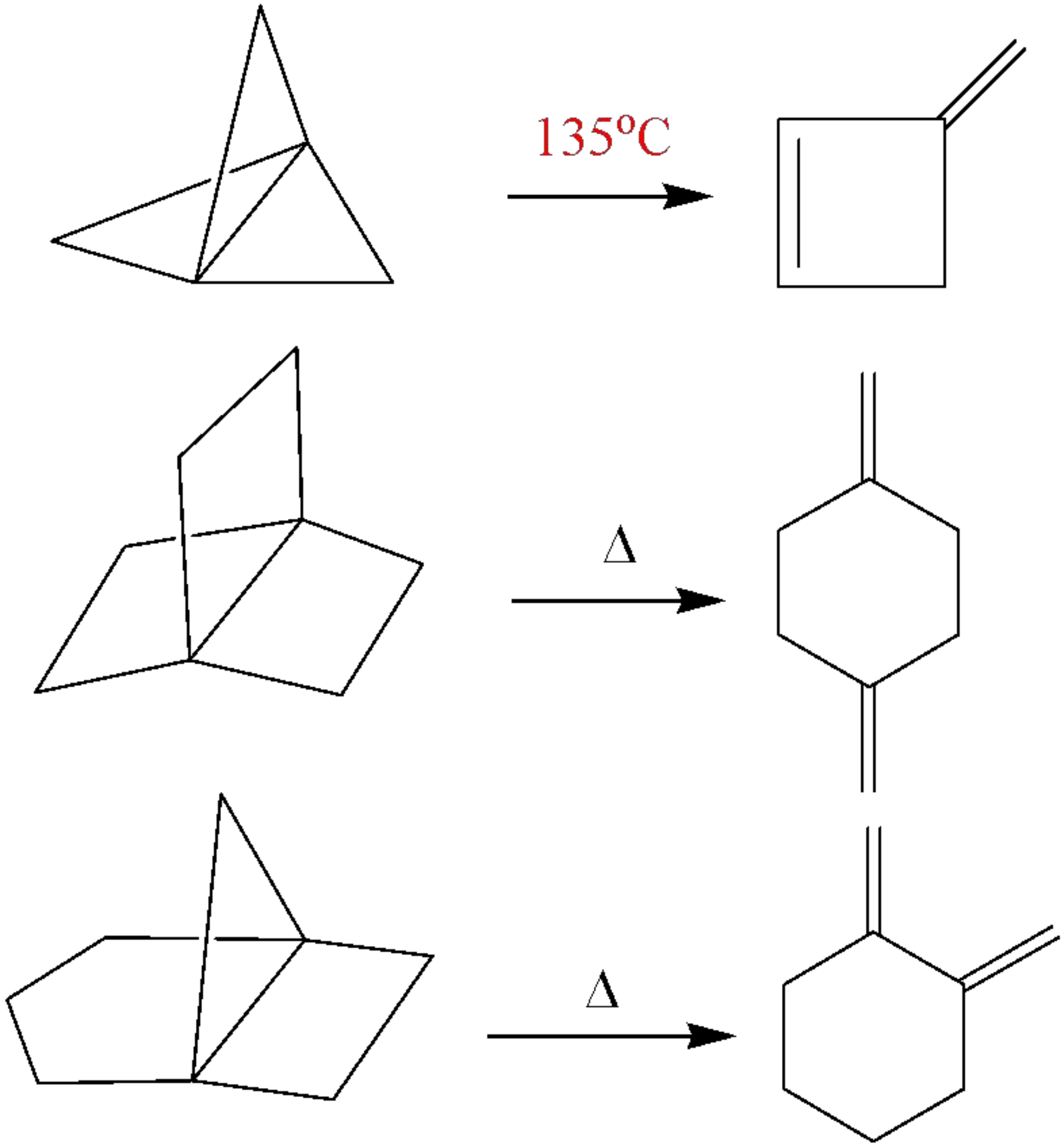




SE, ккал/моль: 93, 67

ab initio 6-31G

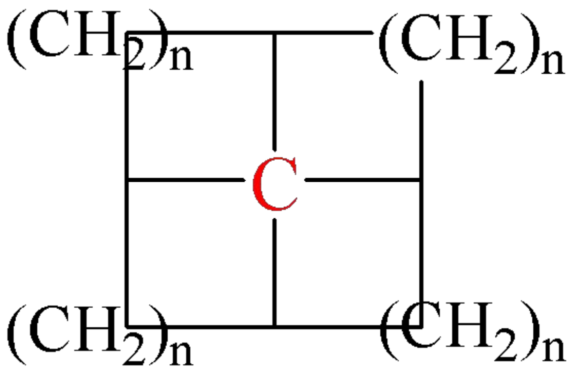
Acc. Chem. Res. **1984**, 379



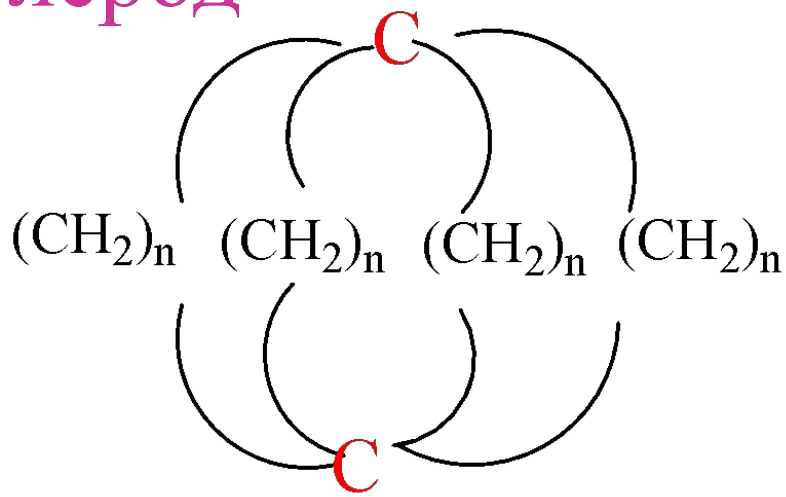
$t_{1/2}$ 1 час, 20°C

$t_{1/2}$ 1 час, 320°C

Планарный углерод



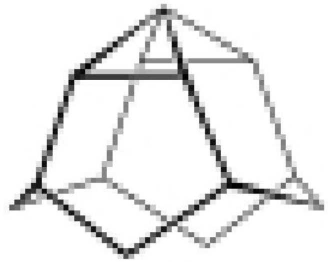
фенестраны



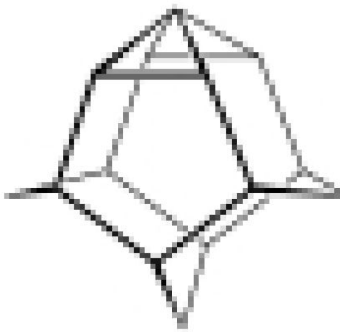
пэддланы

IV

5

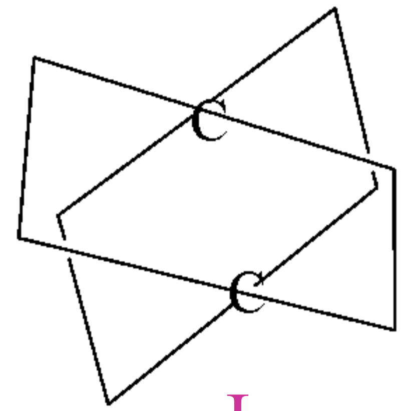


6

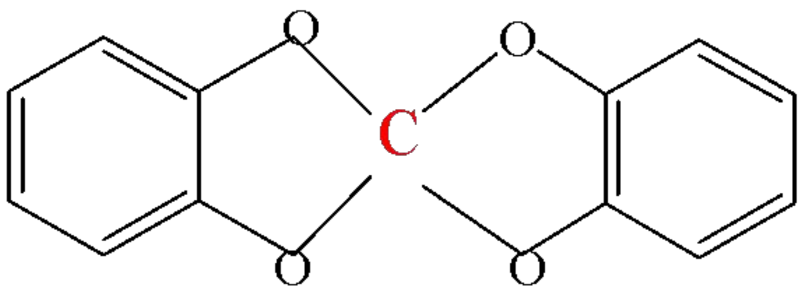


7

В кристалле



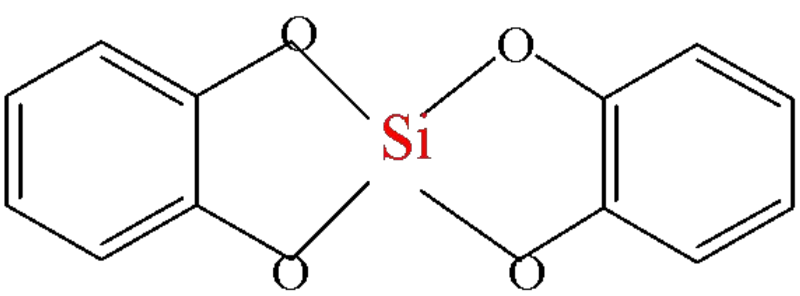
I



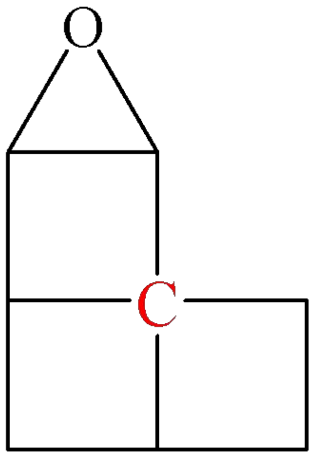
II (тетраэдр)

ab initio (STO-3G)
ΔΔE, ккал/моль

CH_4	240
SiH_4	152



III (планарен)

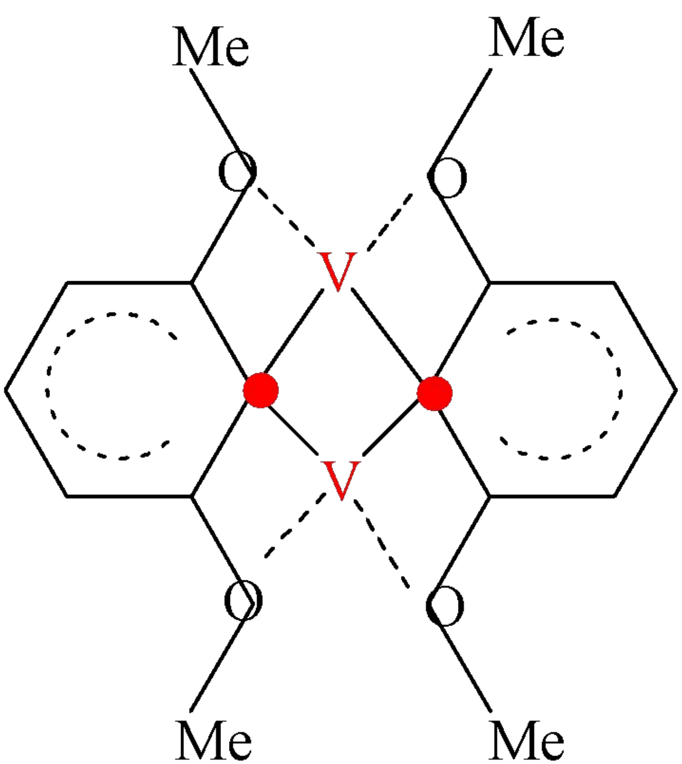


страсбурген

Редакция J. Chem. Res. (1977 г.)

«Первый синтез производного планарного тетракоординированного С»

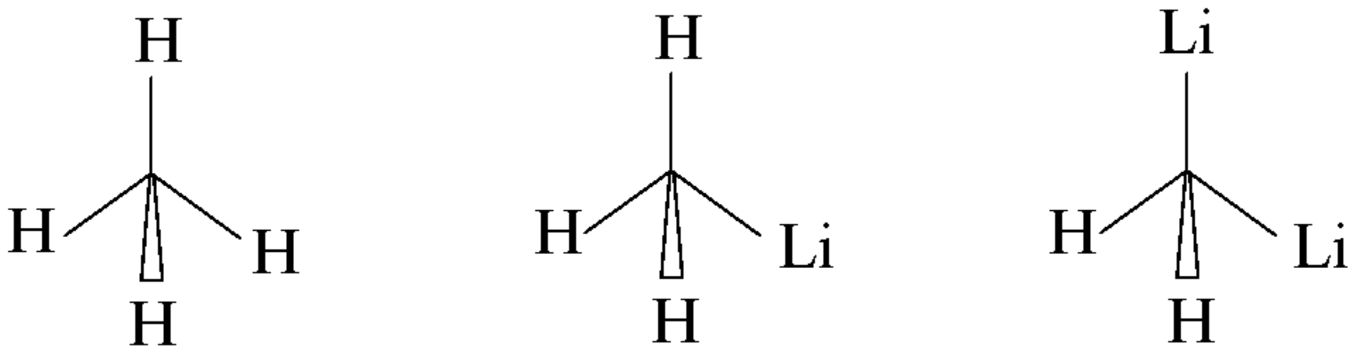
Рислинг, 1977 г.



Cotton, Millar, JACS, 1977

«Планаризация» соединений углерода

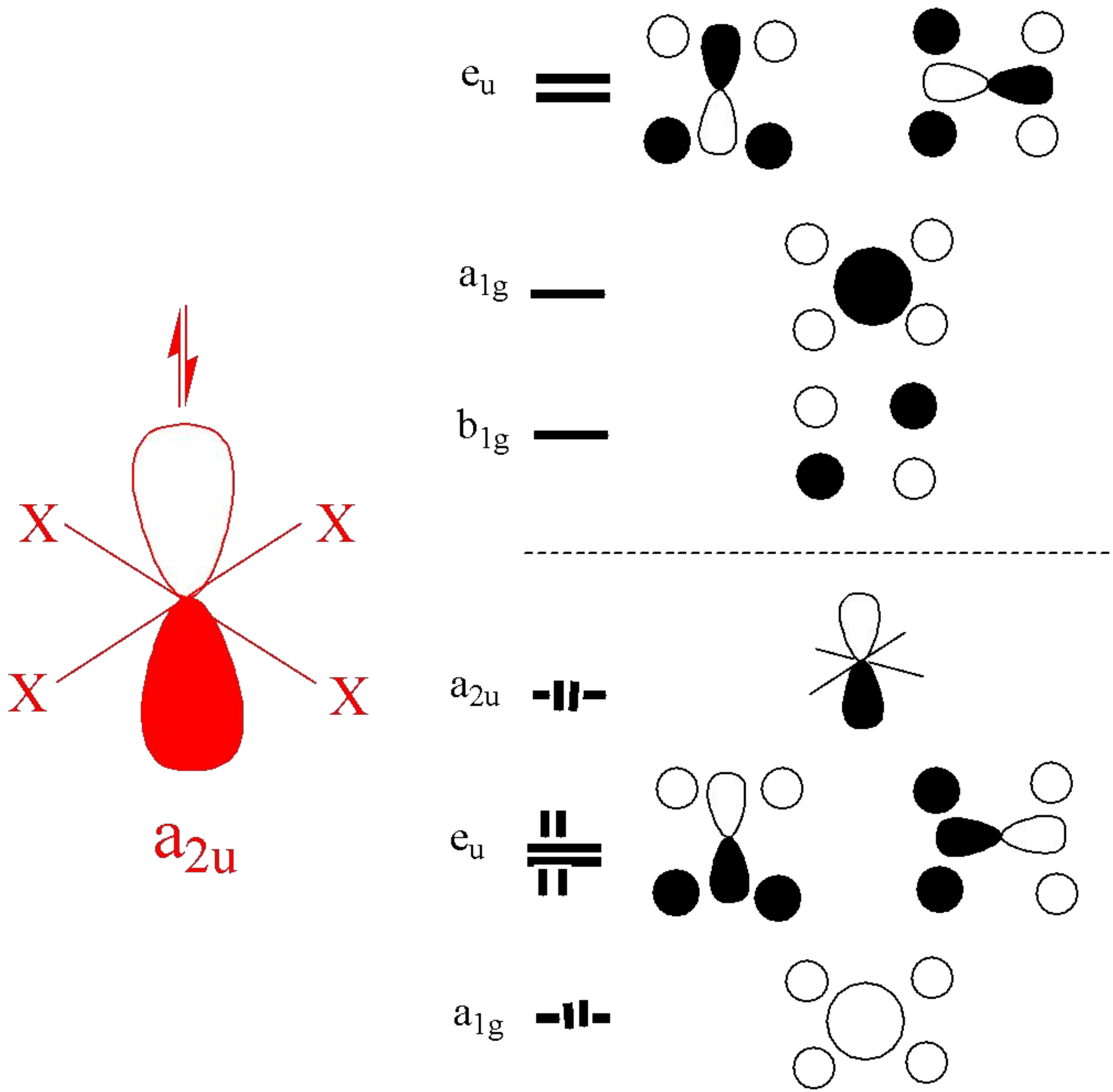
ab initio



ΔΔE, ккал/ моль   122   52   17

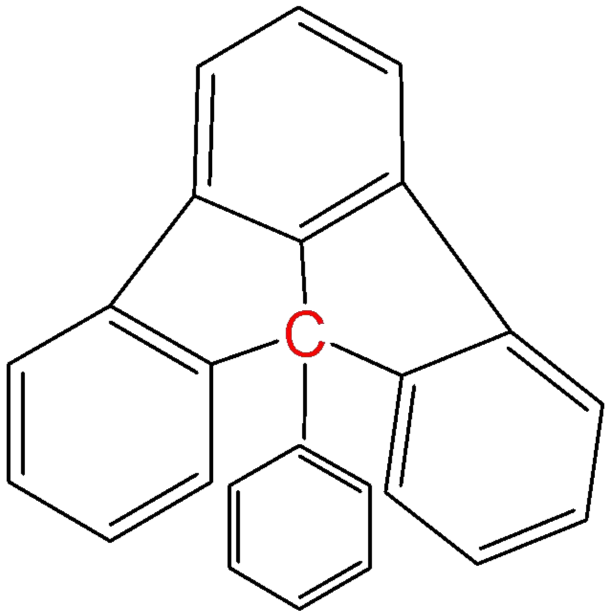
ΔΔE, ккал/ моль   16   -7

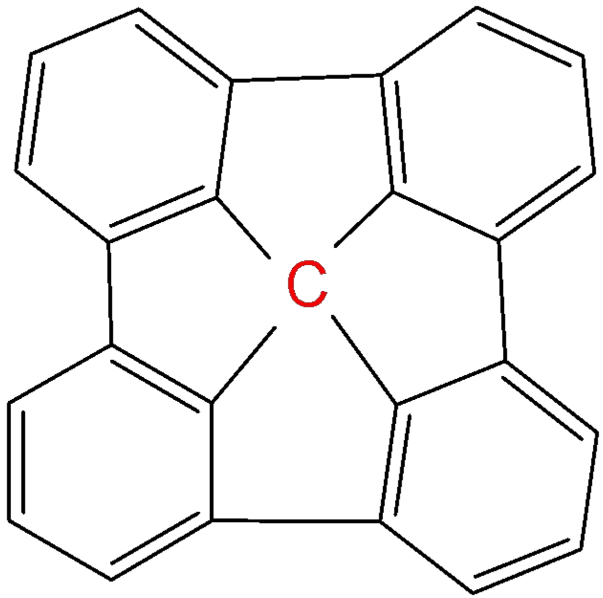
P. Schleyer et al. Ang. Chem. Int., **1997**, 815



e_u
a_1g
b_1g
a_2u
e_u
a_1g
X
X
X
X
a_2u

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

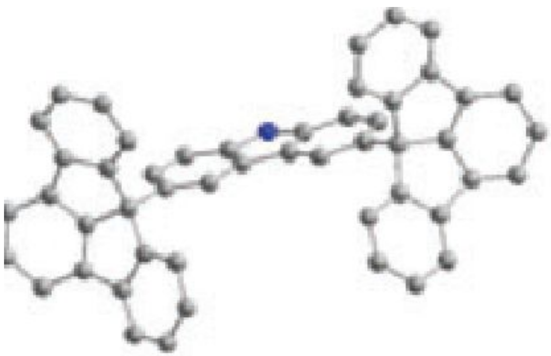




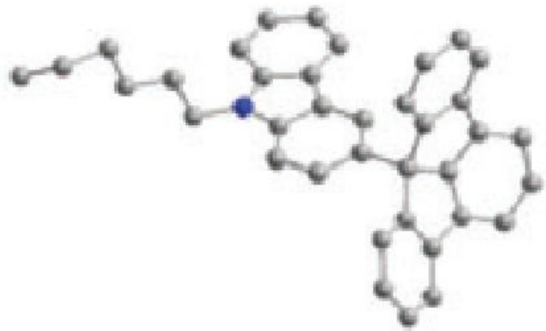
Не синтезированы

Fluradenes

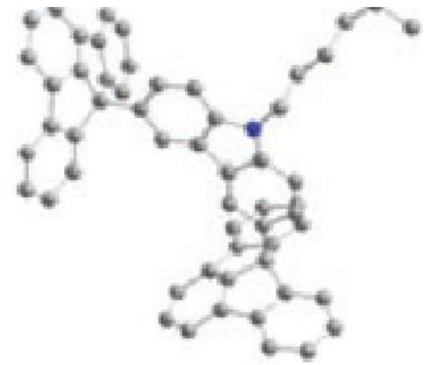
Q. Liu et al., Chem. Comm. **2011**, 2155



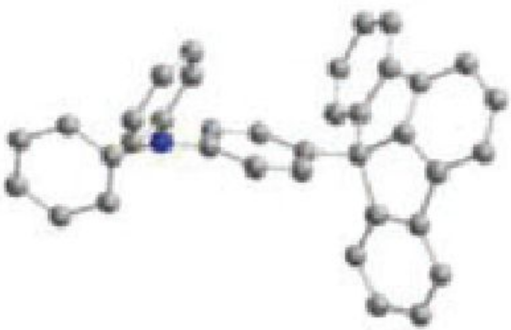
4a



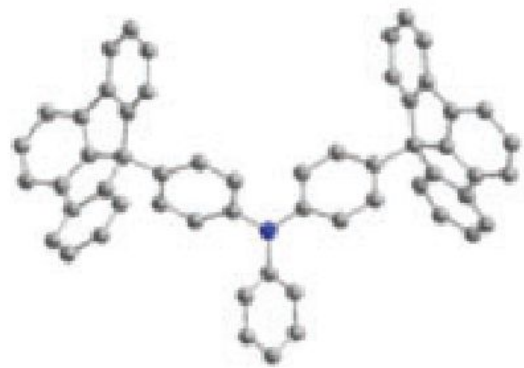
4ba



4bb



4ca



4cb