

# Organic Magnets

Adelina Nemirowski

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Seminar SS 06

# Organic Magnets

- Special features
- Building blocks
- Ways to bulk organic ferromagnets

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# Quantities for Description of Magnetism

*magnetic moment*      *magnetic moment of the spin carrier*

*magnetisation:*

$$\vec{M} = \frac{\vec{\mu}}{V} = \sum_i \frac{\vec{\mu}_i}{V}$$

*magnetic susceptibility:*

$$\chi_m = \frac{\vec{M}}{\vec{H}}$$

*magnetic field*

# Phenomenology: Kinds of Magnetic Behaviour

$$\vec{H}_{ext} = 0$$

short-range spin **order**

**diamagnetic**



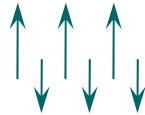
**paramagnetic**



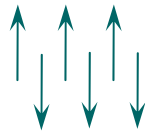
**ferromagnetic**



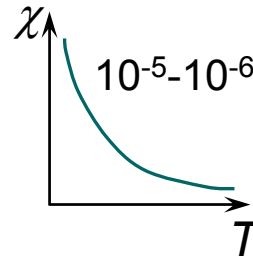
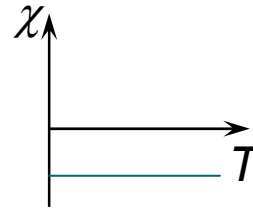
**ferrimagnetic**



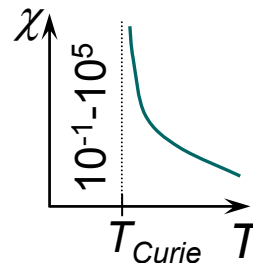
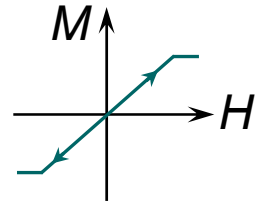
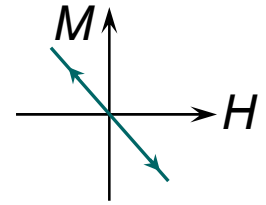
**antiferromagnetic**



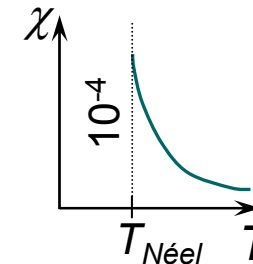
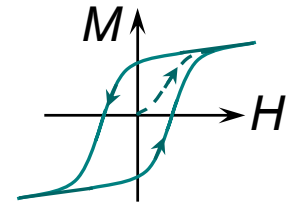
$$\vec{H}_{ext} \neq 0$$



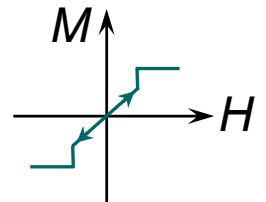
$$\chi = \chi_0 + \frac{C}{T}$$



$$\chi = \frac{C}{T - T_C}$$



$$\chi = \frac{C}{T + \theta_D}$$



Curie-Weiß laws valid above critic parameters:  $T_C$  – Curie and  $T_N$  Néel temperatures;  $\theta_D$  Debye temperature;  $C$  - Curie constant

# Inorganic

- **atomic** entities
- half filled shells
- stable

•  $\alpha$ -Fe ca.  $4 \cdot 10^{23}$  spins

empirics

↓  
theoretical models

*no unified theory* of magnetism

## VS. Magnets

spin carriers

1cm<sup>3</sup> contains

methodics

# Organic

- **molecular** entities
- unsaturated valences  
↓
- **reactive**  
↳ large interspin distances  
↳ small exchange  $E$   
↳  $T_C$  low

• ca.  $10^{21}$ – $10^{22}$  spins

↳  $M = \frac{\mu}{V} = \sum_i \frac{\mu_i}{V}$  low

theoretical proposals

↓  
material design

extrapolation hardly possible

# Characteristics of Ferromagnets

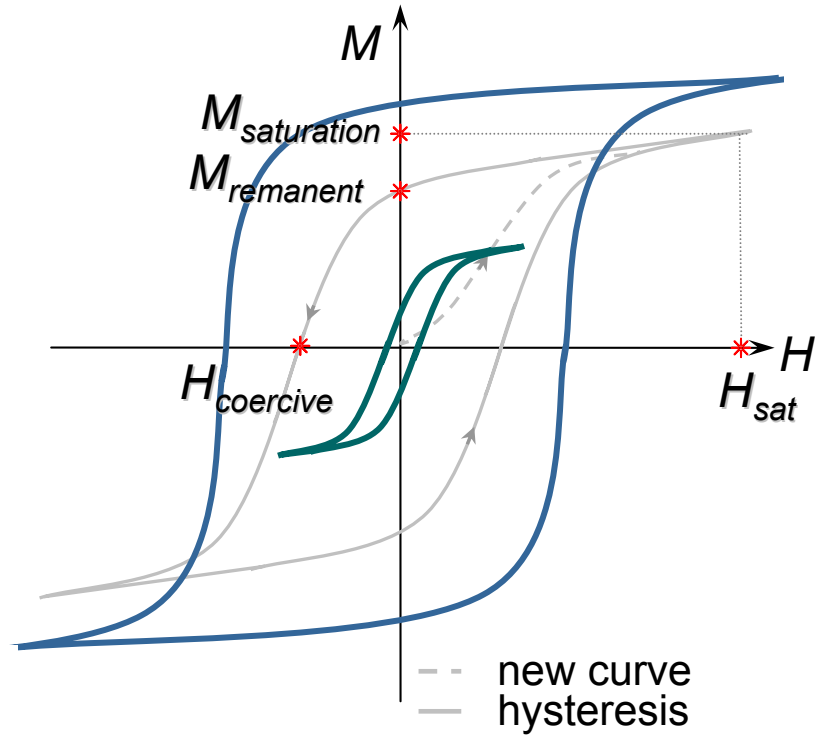
## permanent hard magnets:

\*  $H_{sat}$  high ( $10^4$ - $10^7$  A/m)

\*  $M_{sat} \approx M_{rem}$

## non-permanent soft magnets:

\*  $H_c$  low ( $< 0,1$  A/m)



$$\vec{M} = \frac{\vec{\mu}}{V} = \sum_i \frac{\vec{\mu}_i}{V}$$

$$M_{sat} \propto |T - T_C|^\beta \quad T \leq T_C$$

$$M_{sat} \propto \sqrt[\delta]{H_{coerc}} \quad T \equiv T_C$$

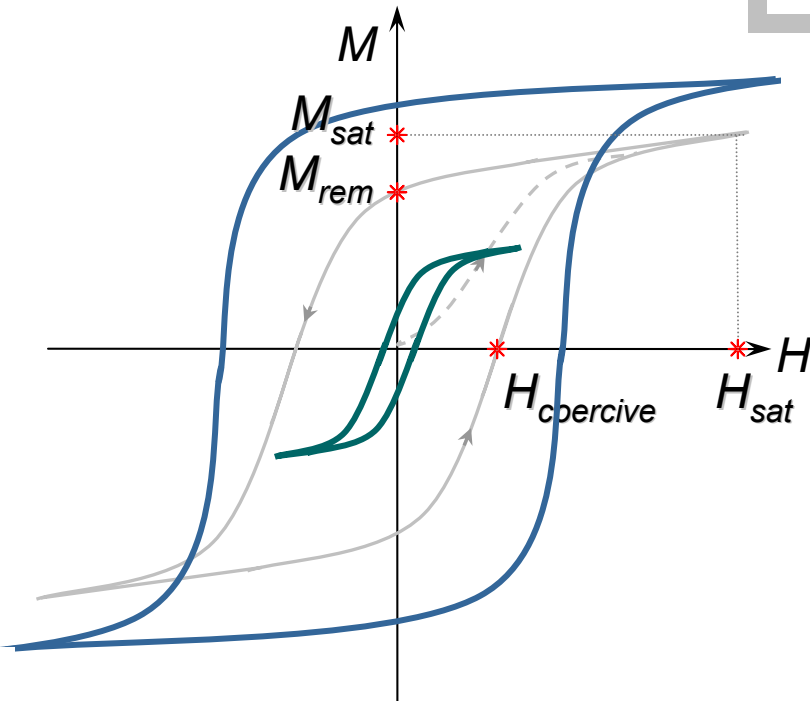
# Characteristics of Ferromagnets      Organic Materials

## permanent hard magnets:

- \*  $H_{sat}$  high ( $10^4$ - $10^7$  A/m)
- \*  $M_{sat} \approx M_{rem}$

## non-permanent soft magnets:

- \*  $H_c$  low ( $< 0,1$  A/m)



- biocompatibility
- flexibility
- low densities

- insulating behaviour

## Applications

### • *in medicine*

- \* magnetic imaging
- \* transducers for implants

### • *to guide or deflect $H_{ext}$*

- \* magnetic shielding of HV electrical lines
- \* core materials in transformers

# Organic Ferromagnets: Rational Design

## Expected Synthetic Advantages

- **environmental** friendliness
- modulation of properties thanks composition-structure relationship
- compatibility with polymers
- **non metallurgical**, low T processing



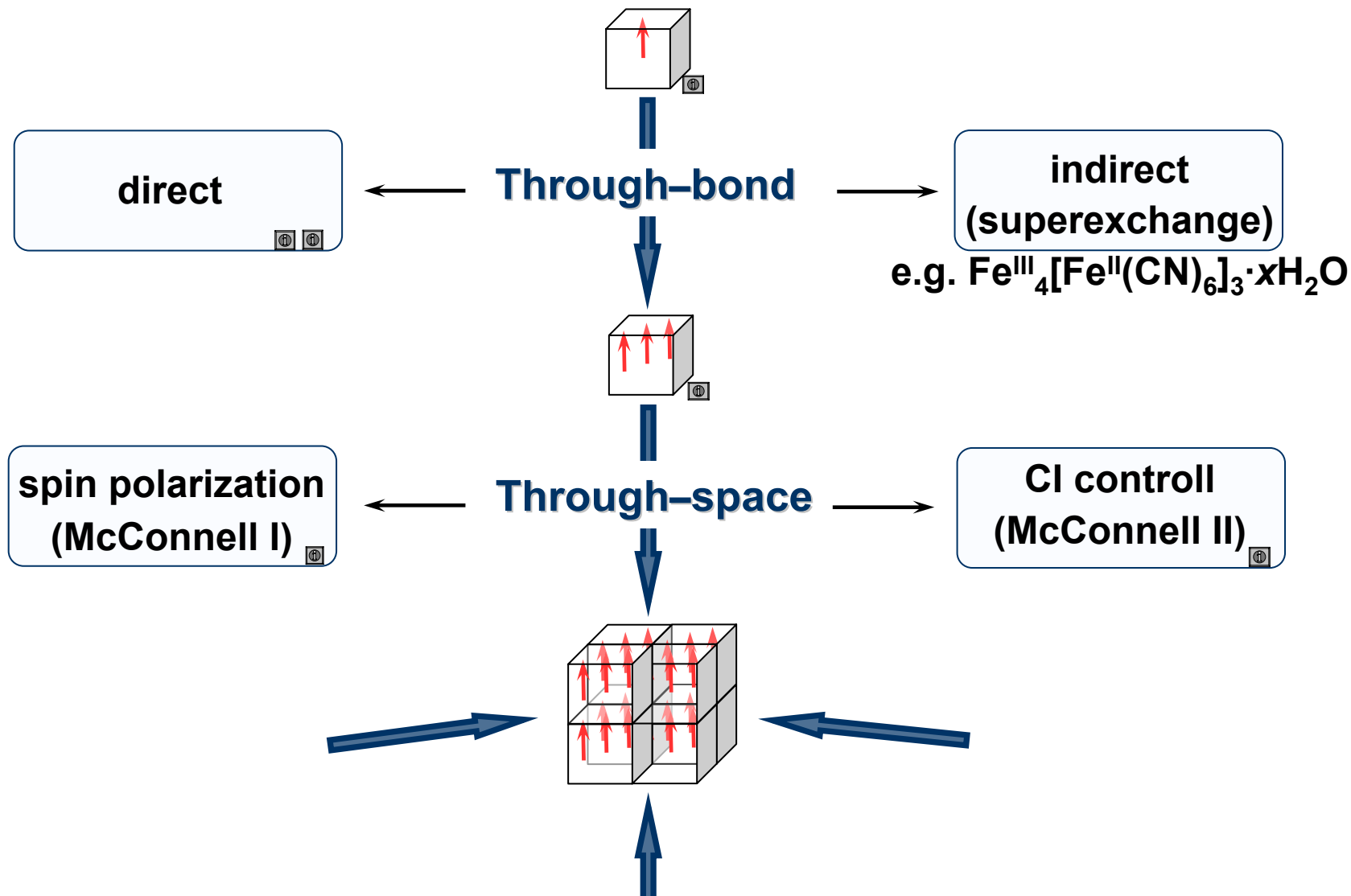
## Encountered Difficulties by Design

- high reactivity
- tendency of single e<sup>-</sup> for bond formation



# Models for Interactions

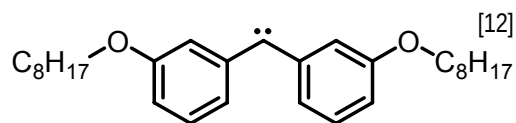
## Providing Ferromagnetic Coupling



# Intermolecular Interactions for 3D Order

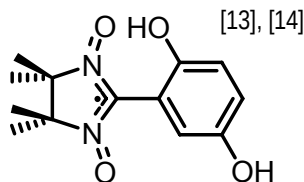
## Arranging forces

### Van der Waals



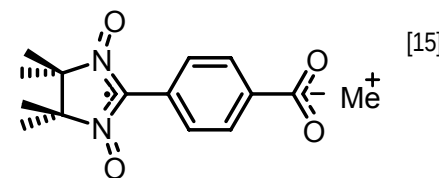
paramagnetic

### H-Bonding



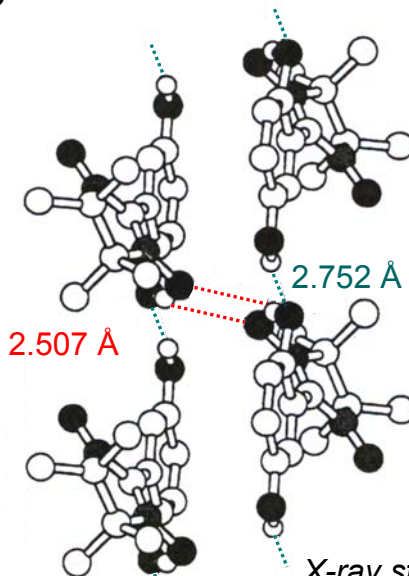
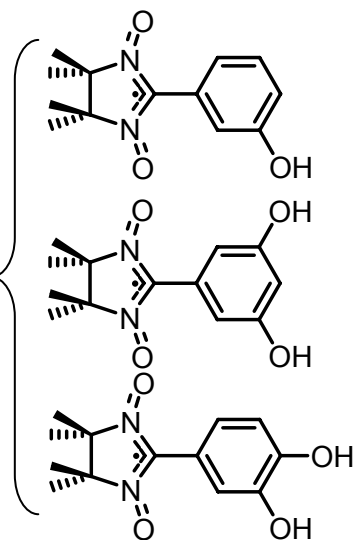
$T_C = 0.5 \text{ K}$

### Coulomb

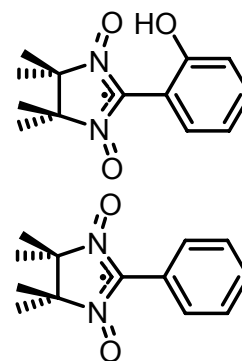


Me = Li, K ferromagnetic  
Na paramagnetic

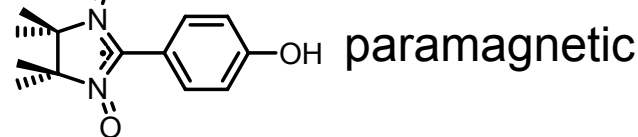
diamagnetic



X-ray structure



$T_C < 0.5 \text{ K}$



paramagnetic

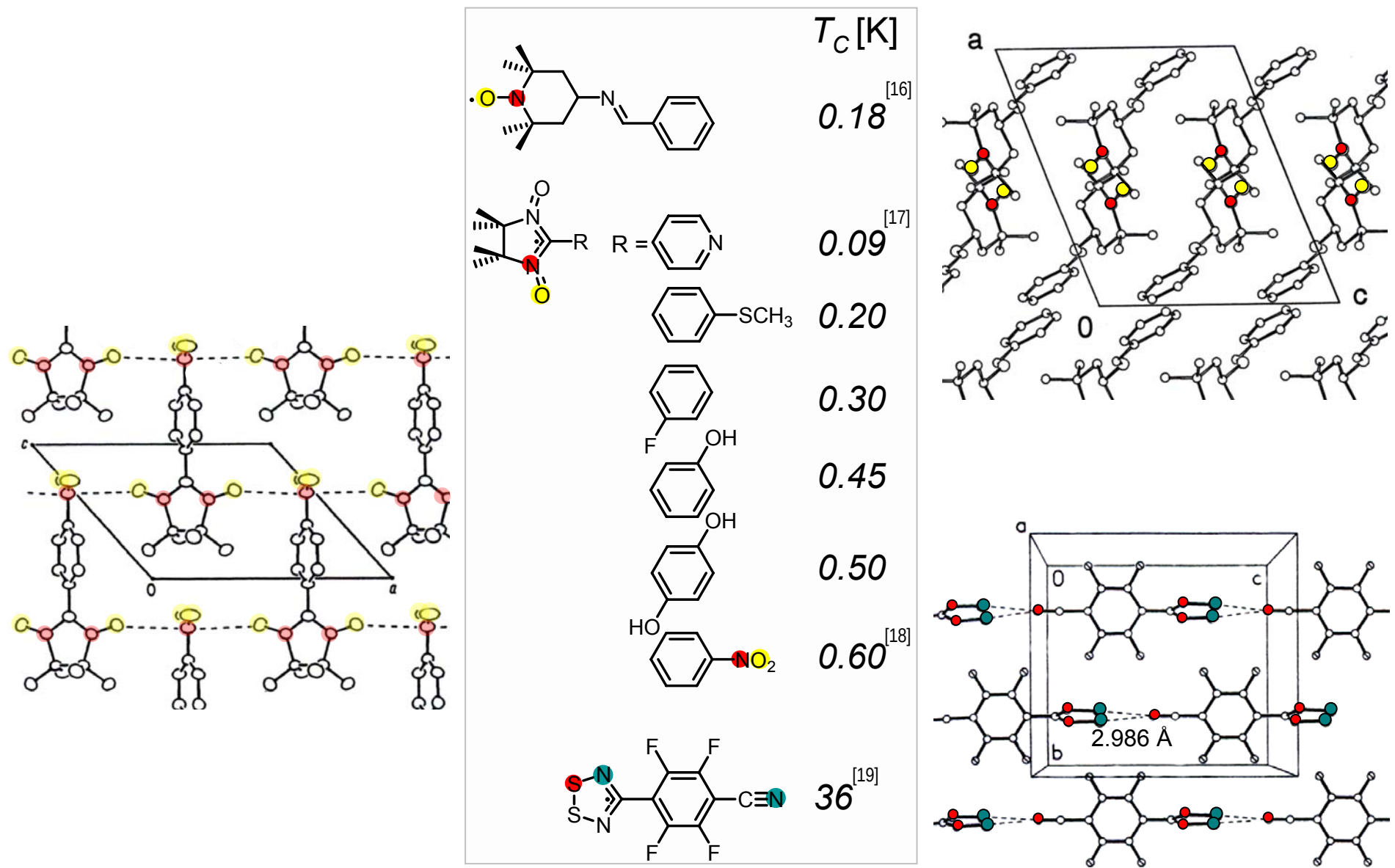
[12] Sugawara, Y.; Murata, S.; Kimura, K.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, 107, 5293

[13] Sugawara, T.; Matsushita, M. M.; Izouka, A.; Wada, N.; Takeda, N.; Ishikawa, M. *J. Chem. Soc. Chem. Comm.* **1994**, 1723

[14] Veciana, J.; Cirujeda, J.; Rovira, C.; Vidal-Gancedo, J. *Adv. Mat.* **1995**, 7, 221

[15] Inoue, K.; Iwamura, H.; *Chem. Phys. Lett.* **1993**, 207, 551

# Synthetic Achievements: Organic Ferromagnets



[16] Nogami, T.; Tomioka, K.; Ishida, T.; Yoshikawa, H.; Yasui, M. *Chem. Lett.* 1994, 29

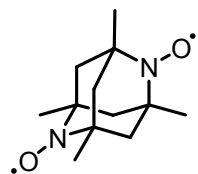
[17] Veciana, J.; Iwamura, H. *MRS. Bull.* 2000, 41

[18] Awaga, K.; Inabe, T.; Nagashima, U.; Maruyama, Y. *J. Chem. Soc. Chem. Comm.* 1989, 1617; Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem Phys. Lett.* 1991, 186, 401

[19] Banister, A. J.; Bricklebank, N.; Lawender, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. R. J.; Palacio, F. *Angew. Chem.* 1996, 108, 2648

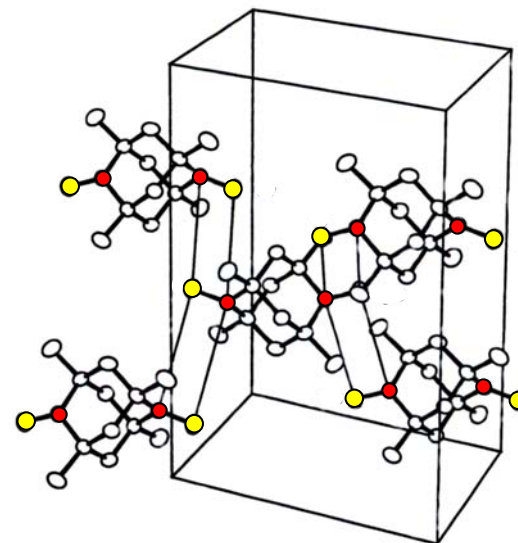
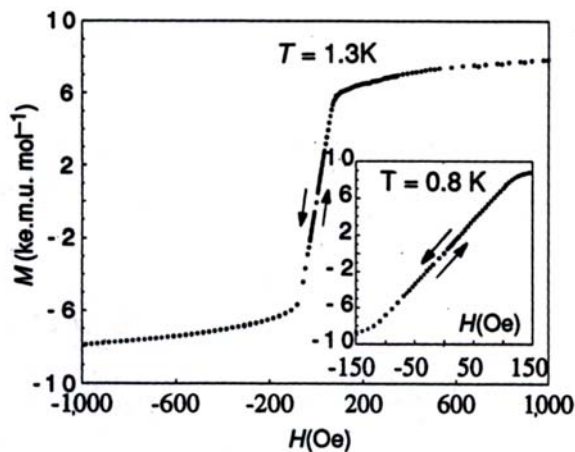
# Non-conjugated Aliphatic Biradical Exhibiting Ferromagnetic Coupling:

N,N'-dioxy-1,3,5,7-tetramethyl-2,6-diazaadamantane



$$T_C = 1.5 \quad [20]$$

no hysteresis:



$$d(\text{NO})_{\text{intremol}} = 5.153 - 4.322 \text{ \AA}$$

# Conclusions

- **no** complete *understanding*, established strategy

↳ trial and error

- "built in" *limitations*:

- reactivity of open-shell moieties

- spin low concentration

↳  $M_{sat}$  small

↳  $T_C$  low

→ *applications*

- not as permanent magnets

- merely as switching units

- state of the art:

- 4 kinds of organic ferromagnetic compounds found

- for each of them less than 10 derivatives

- $T_C$  only for 2 of them exceeds 1 K (36 K)

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# **The Only Incontestable Organic Magnets:**

- ubiquitous
  - extensively studied
  - understood?
-

# The Only Incontestable Organic Magnets:

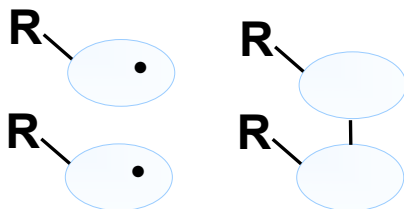
- ubiquitous
- extensively studied
- understood?



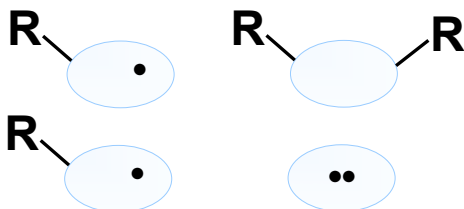
# Spin-Carriers

## Requirements

- kinetic stability towards
  - \* dimerisation

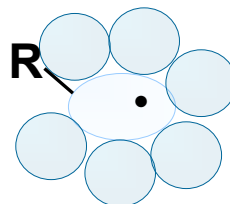


- \* bond cleavage

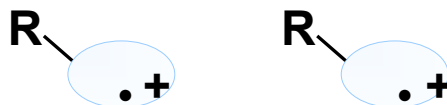


## Strategies

- steric shielding



- introduction of charge



- \* strong bonds, e.g. replacement of C–H with C–Cl

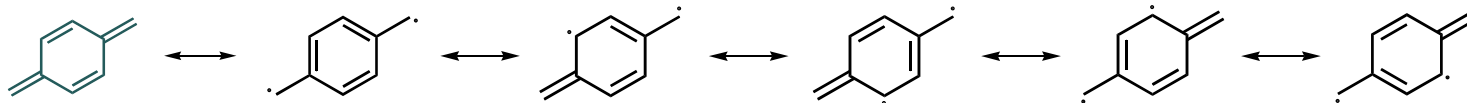
## Drawbacks

- inhibition of magnetic interaction among radical centers

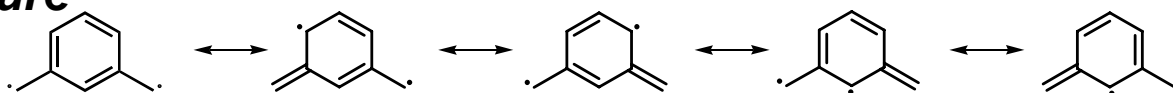
- $n(Q) \uparrow$   
↳ Oxidizability ↓



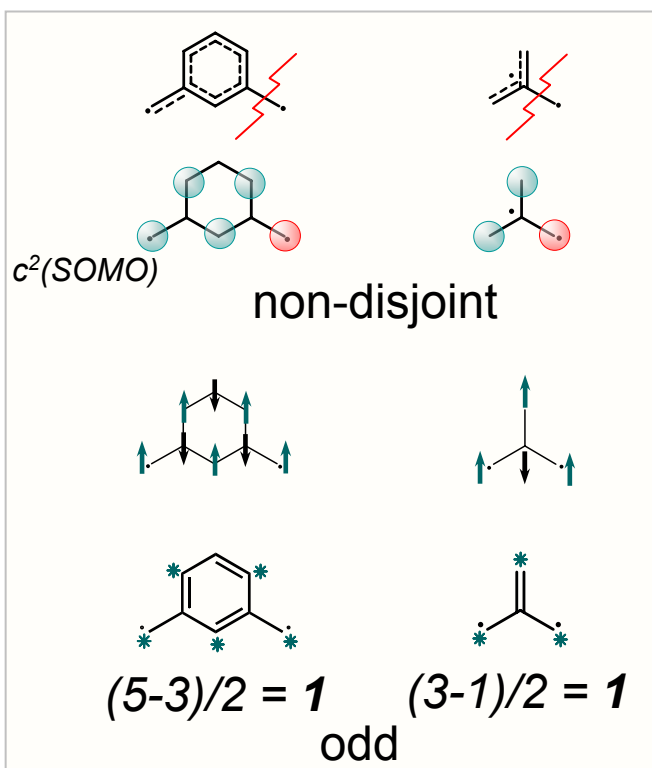
# Conjugated Biradicals: Connectivity $\leftrightarrow$ Multiplicity



**Kekulé structure**



**non-Kekulé structure<sup>[1]</sup>**

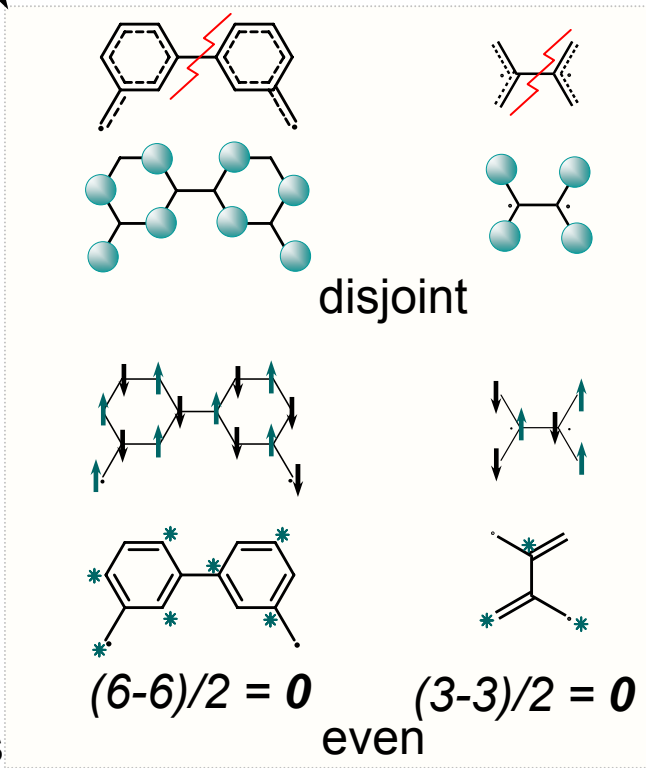


*PMO*  
+ [1]  
*HMO*

*spin-polarization*

$$S = (N_C^* - N_C)/2$$

$N_C$  between radical centers



[1] Hückel, E. Z. Phys. Chem. B 1936, 34, 339

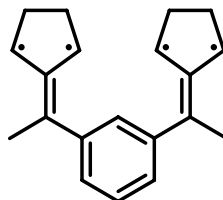
Longuet-Higgins, H. C. J. Chem. Phys. 1950, 18, 265

Borden, W. T.; Davidson, E., R. J. A. Chem. Soc. 1977, 99, 4587



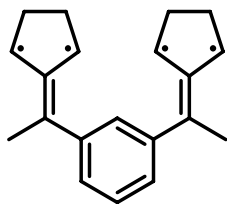
# Limitations of the Modell

prediction for a planar system

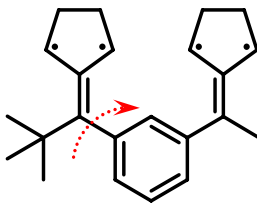


$$S = 2$$

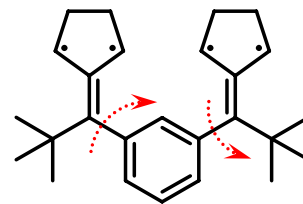
ESR-measurement <sup>[2]</sup>



$$S = 2$$



$$S = 2$$



$$2 \times S = 1$$

twisting prevents the through-bond coupling



nonlinear, rigid backbones,  
e.g. calixarene derivatives



# Paramagnetic Entities

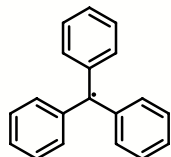
$$S > 1$$

$$S = \frac{1}{2}, 1$$

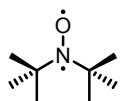
single:

- radicals

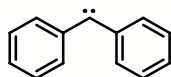
- \* C-centered



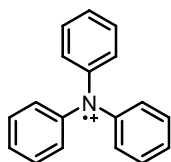
- \* heteroatom-centered



- carbenes (nitrenes)



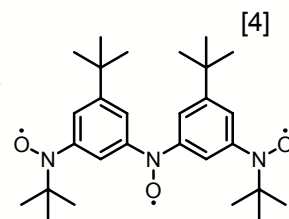
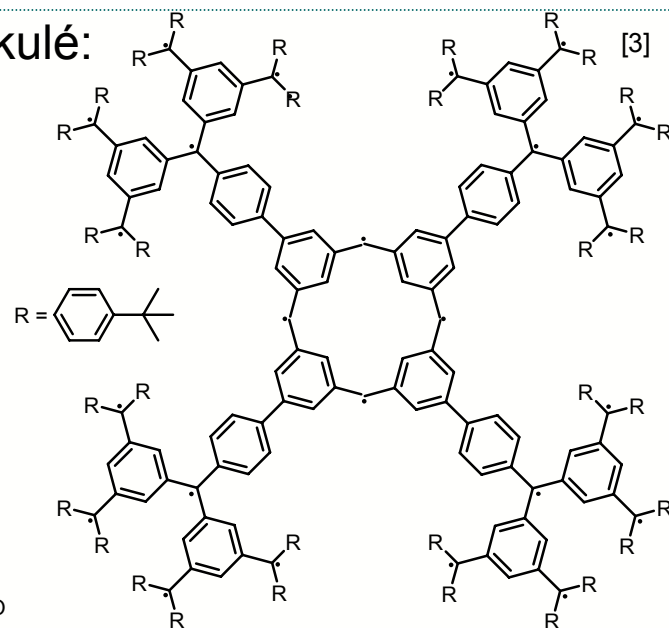
- radical-ions



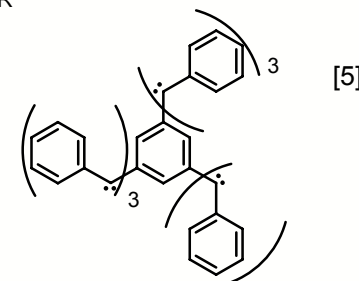
through-bond  
coupling

non-disjoint non-Kekulé:

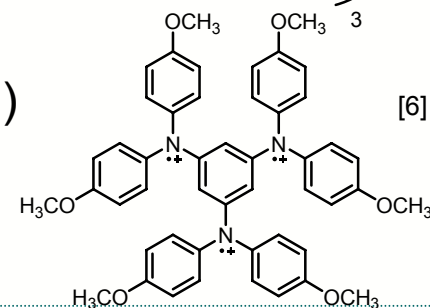
- poly-radicals



- poly-carbenes



- polarons  
(oxidized polymers)



[3] Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* 1995, 117, 13273

[4] Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* 1991, 113, 4238

[5] Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem.* 1993, 105, 900

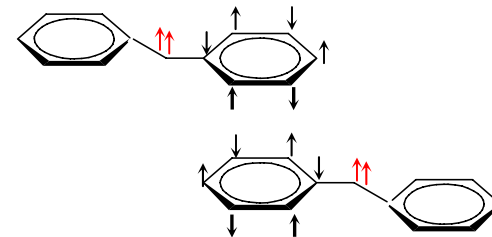
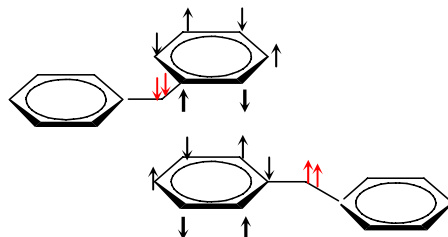
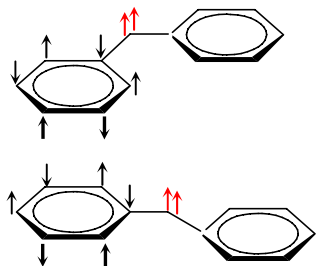
[6] Stickley, K. R.; Blackstock, S. C. *J. Am. Chem. Soc.* 1994, 116, 11576



# Proposed Mechanisms of Ferromagnetic Coupling

## Through-space: spin polarization of covalent bonds

anticipated for an alignment of neighbouring molecules:<sup>[7]</sup>



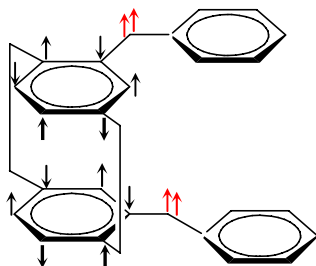
expected:  $S = 2$

$S = 0$

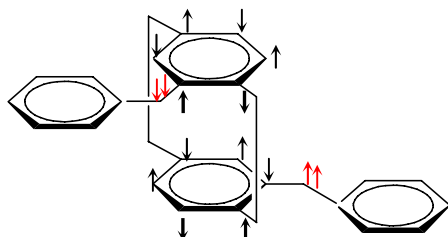
$S = 2$

Testsystems: bis(phenylmethylenyl)[2.2]paracyclophanes<sup>[8]</sup>

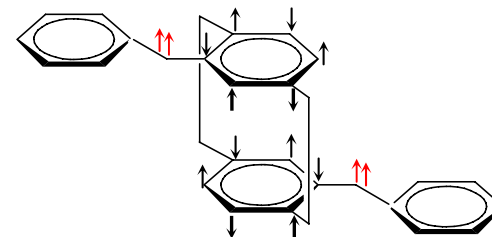
pseudo-*o*-



pseudo-*m*-



pseudo-*p*-



found:  $S = 2$

$S = 0$

$S = 2$

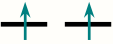
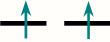
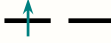
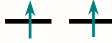
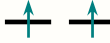
[7] McConnell H. M. *J. Chem. Phys.* 1963, 1910

[8] Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* 1987, 109, 2631

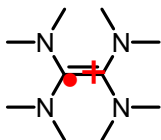
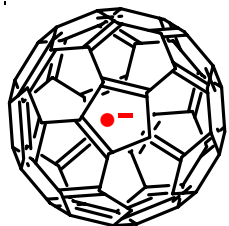


# Proposed Mechanisms of Ferromagnetic Coupling

## Through-space: CI control in CT-salts

| Modell    | FMO occupancies in dominant CIs                                                                                     |                                                                                                                     |                       |                                                                                                                 |                                                                                                                       |
|-----------|---------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|-----------------------|-----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| McConnell | <br><b>A<math>\bullet^-</math></b> | <br><b>D<math>\bullet^+</math></b> | $\longleftrightarrow$ | <br><b>A</b>                   | <br><b>D</b>                       |
| McConnell | <br><b>A<math>\bullet^-</math></b> | <br><b>D<math>\bullet^+</math></b> | $\longleftrightarrow$ | <br><b>A</b>                   | <br><b>D</b>                        |
| Breslow   | <br><b>A<math>\bullet^-</math></b> | <br><b>D<math>\bullet^+</math></b> | $\longleftrightarrow$ | <br><b>A<math>^{2-}</math></b> | <br><b>D<math>^{2+}</math></b>      |
| Torrance  | <br><b>D<math>^+</math></b>        | <br><b>D<math>^+</math></b>        | $\longleftrightarrow$ | <br><b>D</b>                   | <br><b>D<math>^{2+}</math></b>     |
| Wudl      | <br><b>D<math>\bullet^+</math></b> | <br><b>D</b>                       | $\longleftrightarrow$ | <br><b>D</b>                   | <br><b>D<math>\bullet^+</math></b> |

e.g.



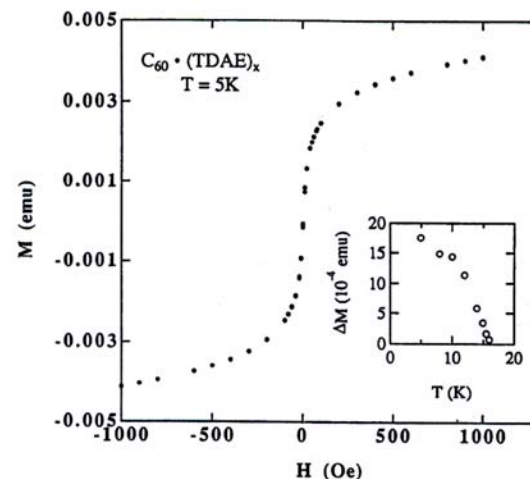
$$T_C = 35.5^{[11]}$$

### Advantage:

- isotropy of Coulomb forces
- regular ordering in *all* directions
- 3D ferromagnetic coupling

### Requirement:

similar redox-potentials for D & A



[9] Nordio, P. L.; Soos, Z. G.; McConnell, H. M. *Annu. Rev. Phys. Chem.* 1966, 17, 237

[10] Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O.; Wudl, F. *J. Am. Chem. Soc.* 1987, 109, 2594

[11] Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D.; *Science* 1991, 301; Tanaka, K.; Zakhidov, A. A.; Yoshizawa, K.; Okahara, K.; Yamabe, T.; Yakushi, K.; Kikuchi, K.; Suzuki, S.; Ikemoto, I.; Achiba, Y. *Phys. Lett. A*, 1992, 201