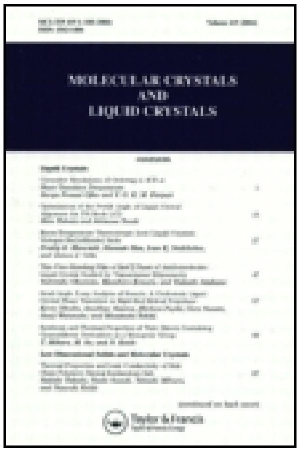


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Role of Hydrogen Bonds in the Propagation of Ferromagnetic Coupling Between High Spin Molecules

Jingping Zhang [a b] , Rongshun Wang [b] & Martin Baumgarten [a]

[a] Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128, Mainz, (Germany)

[b] Department of Chemistry, Northeast Normal University, Changchun, 130024, (P. R. China)

Version of record first published: 04 Oct 2006

To cite this article: Jingping Zhang, Rongshun Wang & Martin Baumgarten (1997): Role of Hydrogen Bonds in the Propagation of Ferromagnetic Coupling Between High Spin Molecules, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 119-123

To link to this article: http://dx.doi.org/10.1080/10587259708044557

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 119–123
Reprints available directly from the publisher
Photocopying permitted by license only

ROLE OF HYDROGEN BONDS IN THE PROPAGATION OF FERROMAGNETIC COUPLING BETWEEN HIGH SPIN MOLECULES

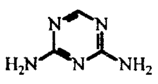
JINGPING ZHANG[1,2], RONGSHUN WANG[2], MARTIN BAUMGARTEN[1*]

[1]Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz (Germany), *author of correspondence; [2]Department of Chemistry, Northeast Normal University, Changchun 130024, (P. R. China)

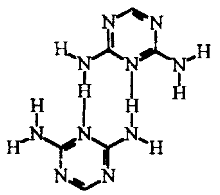
Abstract A new model for ferromagnetic interaction between high spin molecules is proposed where diaminotriazine dications as spin carrying units are hydrogen bonded to a diamagnetic cyanuric acid molecule as spin coupling unit.

INTRODUCTION

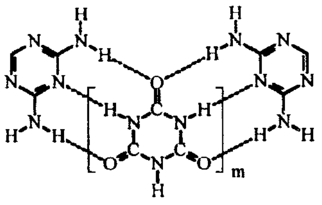
In order to prepare organic ferromagnets from high spin molecules, both intra- and intermolecular ferromagnetic coupling should be fulfilled. The use of hydrogen bonding between radicals for ferromagnetic interactions has most recently been pointed out experimentally for two cases.[1-3] Thereby it was assumed that inter-homomolecular[1] and inter-heteromolecular[2] hydrogen bonding mainly fixes the orientation of the stable radicals. Therefore we now explore the role of hydrogen bonds in the propagation of ferromagnetic coupling in more depth by AM1-CI calculations, especially for answering the question if hydrogen bond formation permits ferromagnetic coupling for inter-homo- and interheteromolecular arrangements. After testing many different examples before, we have now chosen diaminotriazine (DAT) dication biradicals ($\mathbf{1}^{2\bullet+}$) as promising building blocks, which possess a triplet groundstate[4,5] and which can be aggregated through hydrogen bonds with themselves ($\mathbf{2}^{4\bullet+}$, inter-homo-molecular) or with a diamagnetic cyanuric acid (CA) molecule ($\mathbf{3a}^{4\bullet+}$, inter-heteromolecular), respectively. These systems may be viewed as cutoffs from extended aggregates, recently reported by several authors.[6-8]



1



2



3a: m = 1; **3b**: m = 0

COMPUTATIONAL METHODS

The structures of all molecules considered here are optimized fully in combination with CI calculations using the AM1 method, as further outlined in ref. 9. Calculated models are planar and under the constraints of C_2 (**2**) or C_{2v} (**1**$^{2\bullet+}$, **3a**) symmetries. **3b**$^{4\bullet+}$ is explored under the same structure of **3a** or **3a**$^{4\bullet+}$ but without central CA and hydrogen bonds, with the aim to assess the role of inter-heteromolecular hydrogen bonds in the propagation of ferromagnetic coupling for **3a**$^{4\bullet+}$.

RESULTS AND DISCUSSION

In order to reassure the triplet stability in triazine based diradicals we first compared the singlet triplet stabilization of the dication **1**$^{2\bullet+}$ to that of the corresponding *m*-diaminophenylene dication. While the latter case results in mediate triplet stabilization ΔE_{ST} = 0.38 eV of the dicationic centers compared to other possible radical sites, the triazine unit enhances the triplet stabilization dramatically (ΔE_{ST} = 1.07 eV) and makes these radical centers the most stabilized ones in a series of different radical centers being calculated.[5] Since the exact prediction of the absolute energetic gap between high spin and low spin ground state of extended organic multiradicals is hardly feasible even by high quality ab initio methods, we concentrate mainly on the relative trends of stability of high spin multiplicities associated with the variation of molecular alignment, rather than on the absolute numbers as shown earlier.

After complete optimization, all suggested hydrogen bonds are formed in the neutral precursors **2** and **3a**, as shown from the O-N or N-N distances which are lower than the van der Waals radii of 4.1 Å (O····H—N) and 4.2 Å (N·····H—N) [10], respectively.

TABLE I The stabilities of high spin ground states (eV)

	$1^{2.+}$	$2^{4\cdot+}$	$3a^{4\cdot+}$	$3b^{4\cdot+}$
$\Delta E_{S\text{-}T \text{ or } T\text{-}Qui}$	1.07	<0.001	0.01-0.04	<0.001
ΔE_{POMO}	0.61	1.06	1.02	0.82

But while for the interhomomolecular system **2** the N·····H — N distance corresponds to 3.6 Å, in **3** the corresponding interheteromolecular distances lie between 3.0 (O·····H — N) and 3.1 Å (N·····H — N). Charging to the dicationic diaminotriazines then allows to compare the quintet ground state stabilities ($\Delta E_{T\text{-}Qui}$) for the different systems which decreases with the variation of molecular aggregation in the order $\mathbf{3a^{4\bullet}+} > \mathbf{2^{4\bullet}+}$, $\mathbf{3b^{4\bullet}+}$ (table I). To rationalize the calculated results of stability of the ground state multiplicity also the splitting of the partially occupied MO's, the optimized geometries, and the charge and spin density distribution were considered.

TABLE II The charge and spin density distribution on diaminotriazine (DAT) and cyanuric acid (CA) in the proposed trimers

	Charge		Spin density	
	DAT [b]	CA	DAT [b]	CA
3a	0.02	-0.02	-	-
$\mathbf{3a^{4\bullet}+}$	3.95	0.05	4.01	-0.01

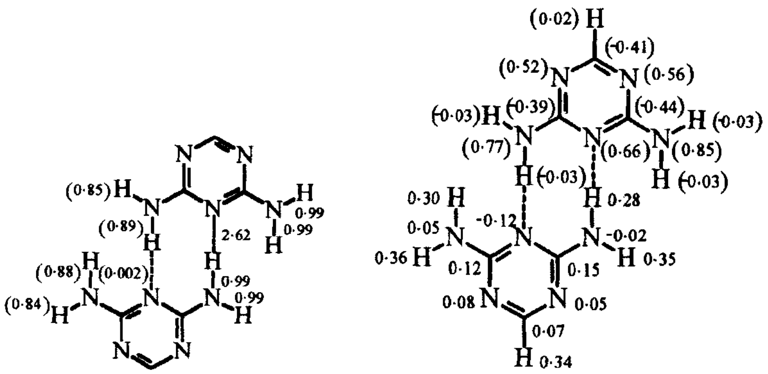


Fig. 1 The optimized distances (in parenthesis) and bond orders of hydrogen bonds and related bonds (a) and the carge and spin densities (in parenthesis) for $\mathbf{2b}^{4+\cdot}$.

For the dimer dication $\mathbf{2}^{4+\cdot}$ charge and spin densities are symmetrically distributed on the two monomeric biradicals, with position of largest charge and spin on the outer, non hydrogen bonded amino groups (Fig. 1).

Though the UHF wavefunction for each monomer implies a pronounced spin density wave (SDW) with alternating large positive and small negative spin densities as in $\mathbf{1}^{2+\cdot}$ only small spin density is found on the hydrogen between two nitrogens. The large splitting of the four POMOs (1.06 eV), partially induced by the asymmetrical spin density distribution in the diaminotriazine subunit may also be responsible for the small quintet stabilization. When looking at the results for the trimer $\mathbf{3a}^{4\bullet+}$ in more depth we find that the charge and spin densities are also symmetrically (C_{2v}) distributed over the aggregate. Meanwhile they reside mainly on the two DAT parts, with largest spin densities on the amino groups (0.85,0.81), which are now more similar than in $\mathbf{2}^{4\bullet+}$, and on the triazine nitrogens (0.66) which forms hydrogen bonds with CA, small amounts of charge and spin are transferred through hydrogen bonds to the CA. In addition when looking at the charge distribution the alternation of positions of large positive and negative contributions are extremely pronounced in the central CA unit. The strong influence of the CA part on the stabilization of the quintet state is further evidenced by comparing $\mathbf{3a}^{4\bullet+}$ with $\mathbf{3b}^{4\bullet+}$, where the same geometries of the DAT molecules is kept but the central CA is taken away. Then the groundstate becomes nearly degenerate, although the splitting of the partially occupied orbitals is lowered (see table 1).

Overall the better stabilization in $\mathbf{3a}^{4\bullet+}$ compared to $\mathbf{2}^{4\bullet+}$ can be explained by the fact that the triple inter-heteromolecular hydrogen bonds formed between each subunit of a trimer can propagate ferromagnetic coupling more effectively than double inter-homomolecular ones between biradical DAT dimer $\mathbf{2}^{4\bullet+}$ (where the NHN distance is considerably larger) and without hydrogen bond $\mathbf{3b}^{4\bullet+}$. The small amounts of charge (0.05) and spin (-0.01) densities transferred through hydrogen bonds to the cyanuric acid may also be responsible for the stronger ferromagnetic coupling in $\mathbf{3a}^{4\bullet+}$.

Although the effective exchange coupling between the radical centers is much smaller than in covalently attached high spin components, it is suggested that hydrogen bonds may be a powerful tool to arrange high spin molecules in a proper way to obtain a bulk magnetization.

REFERENCES

1. T. Sugawara, M. Matsushita, A. Izuoka, N. Wada, N. Takeda, and M. Ishikawa, *J. Chem. Soc. Chem. Commun.* 1723 (1994).
2. J. Veciana, J. Cirujeda, C. Rovira and J. Vidal-Gancedo, *Adv. Mater. 7*, 221 (1995).
3. T. Akita, Y. Mazaki and K. Kobayashi, *J. Chem. Soc. Chem. Commun.* 1861 (1995).
4. K. Müllen, M. Baumgarten, N. Tyutyulkov, and F. Dietz, *Molec. Eng. 4*, 353 (1995).
5. J. Zhang and M. Baumgarten, *Chem. Phys.* in print.
6. A. I. Finkel′shtein and O. S. Rukevich, *Zh. Prikl. Spectrok. 38*, 327 (1983).
7. J. A. Zerkowski, J. C. MacDonald, C. T. Seto, D. A. Wierda, and G. M. Whitesides, *J. Am. Chem. Soc., 116*, 2382-2391 (1994).
8. T. M. Bohanon, S. Denzinger, R. Fink, W. Paulus, H. Ringsdorf, and M. Weck, *Angew. Chem. 107*, 102 (1995).
9. J. Zhang, S. Karabunaliev and M. Baumgarten, *Chem. Phys. 206* ,339 (1996).
10. V. A. Russel, M. C. Ettter, and M. D. Ward, *J. Am. Chem. Soc. 116*, 1941 (1994).