

## DIRECT OBSERVATION OF INTERMOLECULAR INTERACTION FOR ORGANIC MAGNET BY LOW-TEMPERATURE X-RAY DIFFRACTION

Hydrogen bonding plays an important role in the intermolecular interaction, recognition, and conformations of both small and large molecules. In the past decade, it has been recognized that weak C-H $\cdots$ O hydrogen bonds play important roles in the formation of molecular solids [1]. This also confirms the importance of C-H $\cdots$ O contacts for the transmission of magnetic interactions along a particular direction [2]. Now we performed a low-temperature X-ray diffraction (XRD) experiment on radical compounds in order to study such intermolecular interactions by high-resolution X-ray diffraction analysis at very low temperatures. To combine the multipole model of the atom in molecular and topological analyses, we can derive experimental bonding and weak interaction characters from the total electron density, which can be compared with those obtained from theoretical calculations. Taking advantage of the extremely low background of the vacuum chamber camera (VACC) at beamline **BL02B1**, the data quality is greatly improved. Therefore, a precise and accurate multipole model of the molecular solid can be obtained. In this experiment, the X-ray diffraction data was collected at 30 K [3].

The TEMPO (Tetramethyl Piperidin-1-Oxyl) series radical compounds are known to be relatively stable radical compounds. The (PNB-TEMPO) radical molecule as viewed from the *b* axis, is shown in Fig. 1(a), and the difference Fourier map of the molecular plane is shown in Fig. 1(b). In the case of PNB-TEMPO (Para-Nitronyl-4-Benzylideneamino-2,2,6,6-TetraMethyl Piperidin-1-Oxyl), all the residual electron peaks are

found to be in the middle of the interatomic regions, which means that the aspherical electron distribution can be well described in terms of the multipole model.

The molecule has a mirror plane that is perpendicular to the *b* axis; all atoms except the tetra methyl piperidin moiety are on the molecular plane, the distance between layers is 4.769(2) Å, the shortest distance between the different sites of O1 is 5.369(2) Å. The selected distances of the molecular solid are listed in Table 1. The O $\cdots$ H distance is shorter than the sum of the van der Waals' radii (2.72 Å), which makes the packing a pseudo-one-dimensional infinite chain system connected by hydrogen bonds. The spatial arrangement of the chains is in a zigzag configuration along *a* axis. From a polarized neutron diffraction (PND) experiment, we have observed the effect of the magnetic interactions along the chain via the hydrogen bonds, which connect neighboring molecules. The magnetic interactions induced the depletion of the spin density of the oxygen atoms of the hydrogen bonds and some spin density is found to be delocalized among hydrogen-bonded hydrogen atoms. This is reconfirmed by the *ab initio* DFT (Density Functional Theory) theoretical calculations: i.e., the depletion of the spin density of oxygen atoms is quantitatively identified; however, the delocalization of the spin density of the hydrogen-bonded hydrogen atoms can only be qualitatively described. These results clarify the mechanism of the magnetic interactions in these organic magnetic systems.

The theory of atoms in molecules [4] has been

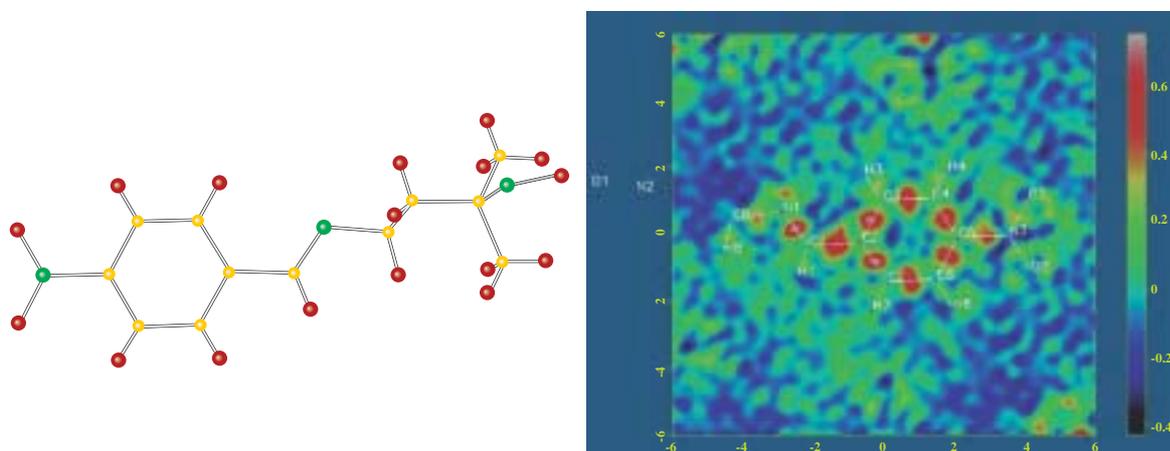


Fig. 1. (a) ORTEP (Oak Ridge Thermal Ellipsoid Plot) drawing of PNB-TEMPO monomer molecule. (b) Residual map of PNB-TEMPO at molecular plane. Data collected at 20 K.

**Table 1.** Selected intermolecular bond distances of PNB-TEMPO at 125 K, 30 K and 20 K (Neutron)

	X-ray (125K)	X-ray (30K)	Neutron (20K)
Bond	Distance	Distance	Distance
O1-H7A	2.423(1)	2.532(1)	2.411(1)
O1-H8B	2.483(1)	2.533(1)	2.446(1)
O1-C7A	3.414(2)	3.394(2)	3.385(1)
O1-C8B	3.553(2)	3.539(2)	3.523(1)

used to describe and characterize intramolecular and intermolecular hydrogen bonding solely from the total charge density for a large set of donor and acceptor molecules. This theory has also provided new insights to intermolecular hydrogen bonding. Even in the characterization of the C-H...O weak hydrogen bond, such interactions can still be recognized by applying topological analysis to an accurate experimentally determined electron density [5]. Bader classifies the hydrogen bond interactions as shared interactions and closed-shell interactions by the sign of  $\nabla^2\rho(r_c)$  and the magnitude of  $\rho(r_c)$ . In addition to the properties associated with the bond critical point, the existence of the bond path between the bonded atoms is also necessary for the characterization of hydrogen bond interactions [6].

Table 2 shows the topological properties associated with the bond critical point of the O...H-C intermolecular hydrogen bond, as determined by experimental X-ray diffraction analysis (a) and theoretical calculation of the dimer (b) and infinite linear chain (c); all three results agree very well with one another. Based on Bader's theory, this interaction can be classified as a closed-shell interaction.

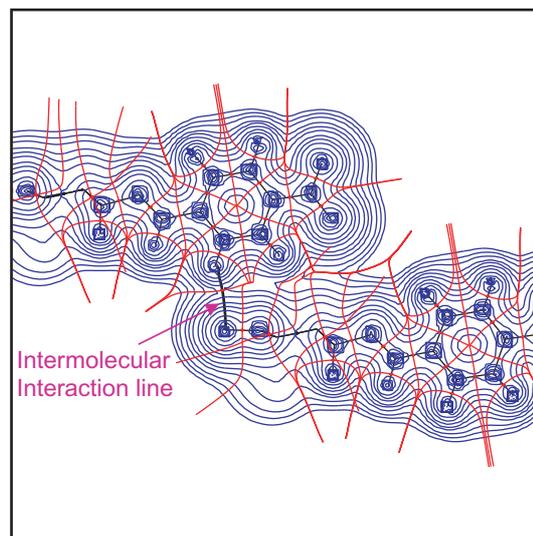
In conclusion, the magnetic interactions between organic radical molecules in a solid along a specific direction are mediated purely through C-H...O hydrogen bonds. Direct observation of such magneto-structural correlation includes use of magnetic measurements, highly accurate single crystal diffraction, and PND measurements.

Yu Wang<sup>a</sup> and Jey Jau Lee<sup>b,\*</sup>

(a) Department of Chemistry, National Taiwan University, Taiwan

(b) National Synchrotron Radiation Research Center, Taiwan

\*E-mail: jjlee@nsrrc.org.tw



**Fig. 2.** Intermolecular interaction evidenced by bond path (black), atom domain (red) superimposed on total electron density (blue) at the molecular plane of PNB-TEMPO dimer.

**Table 2.** Topological properties at bond critical point of O...H-C hydrogen bond on PNB-TEMPO:  
 (a) multipole model  
 (b) Gaussian98/UB3LYP (6-31G(D, P))  
 (c) crystal98/UB3LYP (6-31G(D, P))

Bond/ Bond distance	d1 (Å)	d2 (Å)	$\nabla^2\rho(r_c)$ (eÅ <sup>-5</sup> )	$\rho(r_c)$ (eÅ <sup>-3</sup> )
(a) O1-H7A /2.411(1)	1.516	1.042	0.80	0.040
(b)	1.449	0.974	0.76	0.068
(c)	1.452	0.971	0.75	0.070

## References

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