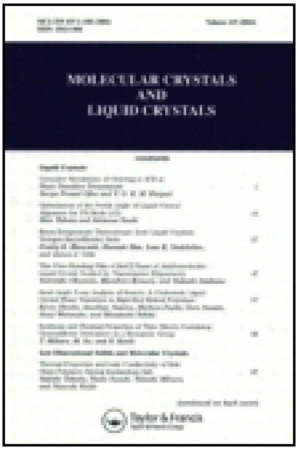

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Spin and Charge Distributions on Cations in $(TMTSF)_2$ ClO_4 and $(TMTTF)_2$ BF_4

Nobumori Kinoshita [a] , Madoka Tokumoto [a] , Hiroyuki Anzai [a] , Takehiko Ishiguro [a] , Tokio Yamabe [b] , Hiroyuki Teramae [b] & Unzi Saito [c]

[a] Electrotechnical Laboratory, Tsukuba Research Center, 305, Japan

[b] Kyoto University, Kyoto, 606, Japan

[c] Institute for Molecular Science, Aichi, 444, Japan

Version of record first published: 17 Oct 2011.

To cite this article: Nobumori Kinoshita , Madoka Tokumoto , Hiroyuki Anzai , Takehiko Ishiguro , Tokio Yamabe , Hiroyuki Teramae & Unzi Saito (1985): Spin and Charge Distributions on Cations in $(TMTSF)_2$ ClO_4 and $(TMTTF)_2$ BF_4 , Molecular Crystals and Liquid Crystals, 119:1, 221-224

To link to this article: http://dx.doi.org/10.1080/00268948508075160

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 221-224
0026-8941/85/1194-0221/$10.00/0

Printed in the United States of America

SPIN AND CHARGE DISTRIBUTIONS ON CATIONS IN $(TMTSF)_2ClO_4$ AND $(TMTTF)_2BF_4$

NOBUMORI KINOSHITA, MADOKA TOKUMOTO, HIROYUKI ANZAI AND TAKEHIKO ISHIGURO
Electrotechnical Laboratory, Tsukuba Research Center 305, Japan
TOKIO YAMABE AND HIROYUKI TERAMAE
Kyoto University, Kyoto 606, Japan
GUNZI SAITO
Institute for Molecular Science, Aichi 444, Japan
(Present Address: The Institute for Solid State Physics, Tokyo 106, Japan)

Abstract Spin and charge distributions on TSF^+ and TTF^+ are evaluated based on the molecular orbital calculations by fitting the anisotropic observed g factors of $(TMTSF)_2ClO_4$ and $(TMTTF)_2BF_4$.

INTRODUCTION

$(TMTCF)_2X$ salts, (C: chalcogens, X: anions), exhibit a variety of electronic and magnetic properties such as superconductivity, charge density wave, spin density wave and so on depending on the contained chalcogens and/or anions.[1] To obtain a full understanding of these substances, it is important to know the molecular orbitals (MO's) of a TMTCF cation, because π-electrons on the cation dominate the electronic properties of $(TMTCF)_2X$.

In this paper we present the spin and charge distributions on $(TMTSF)_2ClO_4$ and on $(TMTTF)_2BF_4$ which are derived from the fitting of the calculated ESR g factors to the observed ones which show the characteristic anisotropy.[2]

EXPERIMENTS AND CALCULATIONS

X-band ESR experiments have been carried out for $(TMTSF)_2ClO_4$ at

4.2 K[2] and for $(TMTTF)_2BF_4$ at room temperature. (Since $(TMTSF)_2ClO_4$ exhibits a broad ESR line at room temperature, a precise g factors were decided by the low temperature experiments.)

We found also that the g factors of $TMTSF^+$ in solution are consistent with those of $(TMTSF)_2ClO_4$.[2] This means that the $TMTSF^+$ represent the cation in $(TMTSF)_2ClO_4$ as far as the ESR g factors are concerned.

Based on this fact we calculate MO's of TSF^+ and those of TTF^+ instead of the cations in $(TMTSF)_2ClO_4$ and $(TMTTF)_2BF_4$ so that the calculation can be tractable, using the semi-empirical SCF MO method for the valence electron systems.[3] For simplicity we neglected the d-orbital contribution of Se and S. Parameters used in the calculation are quoted from Yonezawa et al.[3] except a constant K appeared in the core resonance integral and the values of the ionization potential I_p and of the electron affinity E_a of Se and S. Used values of I_p and E_a of S which were decided by the best fitting of the calculated g factors to the observed ones are 13.32 eV and 12.32 eV, respectively. Parameters for Se are given

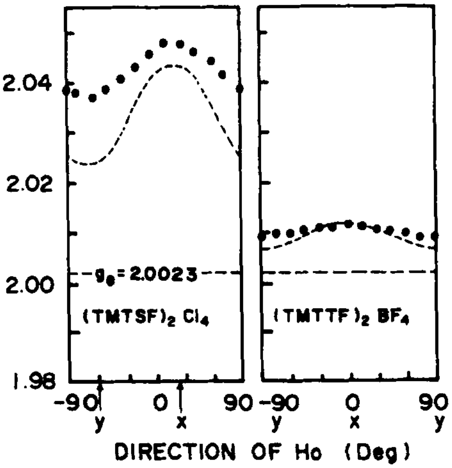

FIGURE 1 Angular dependences of the observed (●●) and the calculated (---) g factors for $(TMTSF)_2ClO_4$ and $(TMTTF)_2BF_4$.

in Ref. 2. For the geometry of TTF^+, the data in Ref. 4 are used.

Figure 1 shows the angular dependences of the observed and calculated g factors for $(TMTSF)_2ClO_4$ and $(TMTTF)_2BF_4$ in the molecular plane of the fulvalene. "x" is the axis parallel to the longest axis of the fulvalene and "y" is perpendicular to "x". The difference in the g factor between $(TMTSF)_2ClO_4$ and $(TMTTF)_2BF_4$ can be explained in terms of the difference in the spin orbit coupling constant between Se and S atoms.

With the computed MO's, the spin distribution (σ_k) and the charge distribution (ρ_k) of atom k are obtained as follows;

$$\left.\begin{aligned} \sigma_k &= C_{k0}^2 \\ \rho_k &= C_{k0}^2 + 2\sum_n^{occ} C_{kn}^2 , \end{aligned}\right\} \qquad (1)$$

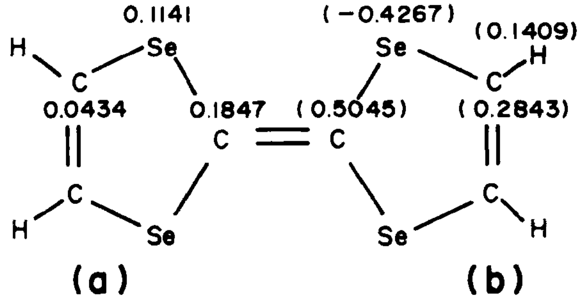

FIGURE 2 Spin (a) and charge (b) distributions on TSF^+.

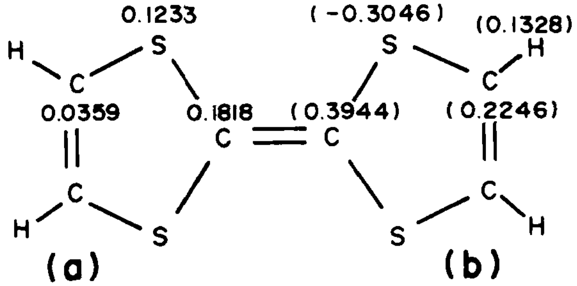

FIGURE 3 Spin (a) and charge (b) distributions on TTF^+.

where C_{k0} and C_{kn} are the coefficients of the atomic orbitals which constitute MO's and the suffixes "0" and "n" represent the single occupied MO (SOMO) and the other MO's except SOMO.

RESULTS

The derived spin and charge distributions in the TSF^+ cation are shown in Fig. 2. Figure 2(a) (left half of the fulvalene) shows the spin distribution and Fig. 2(b) (right half) shows the charge distribution (in the parenthesis). The equivalent sites in TSF^+ have the same distribution.

Figure 2 shows that the spins on TSF^+ is more localized on the inner carbon site rather than the selenium site. On the other hand, negative charges are localized at the selenium site while positive charges distribute on the other sites.

For comparison we show also the spin and charge distributions on a TTF^+ cation in Fig. 3. We found that TSF^+ and TTF^+ resemble in spin and charge distributions.

REFERENCES

1. S.S.P. Parkin, F. Creuzet, M. Ribault, D. Jerome, K. Bechgaard and J.M. Fabre, Mol. Cryst. Liq. Cryst., 79, 249 (1982).
2. N. Kinoshita, M. Tokumoto, H. Anzai, T. Ishiguro, G. Saito, T. Yamabe and H. Teramae, J. Phys. Soc. Jpn., 53, 1504 (1984).
3. T. Yonezawa, H. Konishi and H. Kato, Bull. Chem. Soc. Jpn., 42, 933 (1969).
4. P.J.L. Galigne, B. Liautard, S. Peytavin, G. Brun, M. Maurin, J.M. Fabre, E. Torreilles and L. Giral, Acta Cryst., B35, 1129 (1979).