Magnetic Susceptibility and Crystal Structure of 1,5-Diphenyl-3-(4-chlorophenyl)verdazyl Radical[1)]

Nagao AZUMA,*, ** Kanji TSUTSUI,† Yozo MIURA,†† and Taiichi HIGUCHI*, †

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606
†*Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558*
††*Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku Osaka 558*

(Received March 4, 1981)

The magnetic susceptibility of 1,5-diphenyl-3-(4-chlorophenyl)verdazyl (Cl-TPV) has been measured on a powder sample in the temperature region between 1.8 and 80 K. It exhibited a round maximum at 21.0 K; this temperature is the highest among those observed for verdazyl monoradicals. The susceptibility can be well described by the Heisenberg linear chain model; the estimated exchange interaction parameter is $J/k=-16.4$ K. The crystal structure of Cl-TPV has been determined by means of X-ray diffraction. The crystal is orthorhombic, with the space group of Pbca and with $a=22.041(5)$, $b=7.166(4)$, $c=21.379(5)$ Å, and $Z=8$. The molecules are arranged in a column along the b axis. The exchange interaction has been discussed based on the crystal structure and the spin density distribution.

Electron spin-spin exchange interaction in a radical crystal is dependent on the crystal structure and the spin density distribution. In order to obtain the exchange interaction as a function of the interatomic distance and the spin density, 1,3,5-triphenylverdazyl (TPV) and its methyl derivatives, such as 1,3,5-triphenyl-6-methylverdazyl and 1,3-di-*p*-tolyl-5-phenylverdazyl (DTPV), have been studied to determine their magnetic susceptibilities, spin densities, and crystal structures.[2)] The C-phenyl ring in TPV lies in the nodal plane of the highest-occupied molecular orbital,[3)] so the replacement of the hydrogen atom in that ring scarcely perturbs the spin density distribution. Thus, a chlorine atom has been introduced into *para*-position and the molecular packing has been modified from that of TPV. The exchange interaction estimated from the magnetic susceptibility of this 1,5-diphenyl-3-(4-chlorophenyl)verdazyl (Cl-TPV) is the strongest among the verdazyl monoradicals examined. In order to understand the exchange interaction of Cl-TPV and to try the tractable function in Ref. 2, the crystal structure of this radical has been determined by means of X-ray diffraction.

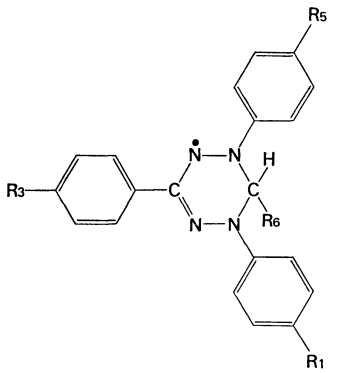

Fig. 1. Chemical structures of verdazyl radicals.

Radical	R_1	R_3	R_5	R_6
TPV	H	H	H	H
Cl-TPV	H	Cl	H	H
DTPV	CH_3	CH_3	H	H

Experimental

Cl-TPV was prepared from *p*-chlorobenzaldehyde, aniline and formaldehyde.[4)] The dark green crystals, elongated along the b axis, were purified several times through recrystallization from a mixed solution of acetone and methanol.

The magnetic susceptibility was measured on the powdered sample by means of a magnetic torsion balance.[5)] The temperature was determined using an AuCo–Cu thermocouple and a carbon resister. Manganese Tutton salt was used for the calibration of the thermometers and the field intensity.

ESR spectra of Cl-TPV and TPV in toluene were recorded on an X-band spectrometer at room temperature, in order to estimate the difference in the spin density distributions of these radicals.

The unit-cell parameters were obtained from the photographic data. The crystal data are summarized in Table 1. The Weissenberg intensity data (*h0l*—*h5l*, 0*kl*—1*kl*) were collected with Cu $K\alpha$ radiation and corrected for Lorentz and polarization effects. There were 2326 independent reflections, of which 1741 were regarded as observed.

Table 1. Crystal data of Cl-TPV

Molecular formula	$C_{20}H_{16}N_4Cl$
Molecular weight	347.8
Melting point	144—145 °C
Crystal system	Orthorhombic
Space group	Pbca
Cell dimensions;	
a/Å	22.041(5)
b/Å	7.166(4)
c/Å	21.379(5)
V/Å^3	3376.5
Z	8
Density (calcd)/g cm^{-3}	1.368
Density (obsd)/g cm^{-3}	1.35

** Permanent address: Laboratory of Chemistry, Faculty of General Education, Ehime University, Matsuyama, Ehime 790.

Results of Magnetic Measurements

The susceptibility data were corrected for the diamagnetic contribution using Pascal's constants.[6] The paramagnetic molar susceptibility, χ_m, is shown in Fig. 2. The susceptibility follows the Curie-Weiss law with a negative Weiss constant, $\theta = -18.4$ K, in the high temperature region. However, the susceptibility deviates from the Curie-Weiss law at low temperatures, and it shows a round maximum with a value of $\chi_{max} = 6.70 \times 10^{-3}$ cgs emu mol^{-1} at $T_{max} = 21.0$ K.*** When the temperature is lowered further, the susceptibility decreases towards a finite value at 0 K. The radical concentration, as determined from the susceptibility data at high temperatures, is 100%, with an experimental error of 3%.

The ESR spectrum of TPV exhibited nine line splittings, with the hyperfine coupling constant of 0.59 mT due to the nearly equivalent four nitrogen nuclei; the splittings from protons were unresolved. On the other hand, the spectrum from Cl-TPV showed many incompletely resolved splittings due to the protons, as is shown in Fig. 3. However, the spacing of 0.59 mT of the nine line splittings was unchanged.

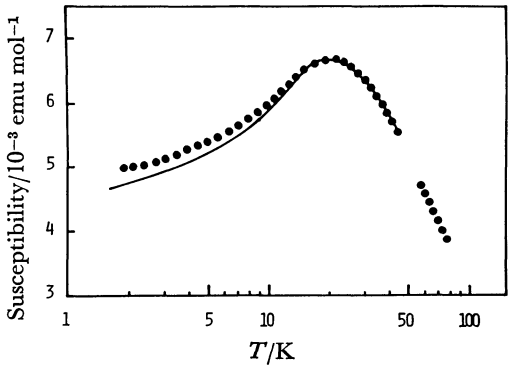

Fig. 2. Paramagnetic molar susceptibility of Cl-TPV powder. Solid circles show the experimental data and solid line is the susceptibility of the Heisenberg linear chain.

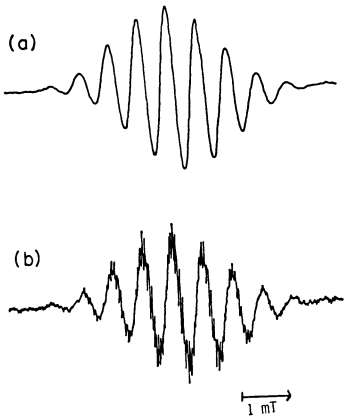

Fig. 3. ESR spectra of TPV (a) and Cl-TPV (b) in toluene.

***The value of the molar susceptibility in m^3 mol^{-1} (SI) can be obtained by multiplying the value in emu mol^{-1} (cgs) by $4\pi \times 10^{-6}$.

Structure Determination and Refinement

The crystal structure was solved by the direct method using a program written in our laboratory. The positions of all the 25 non-hydrogen atoms located on an E map were refined by the blockdiagonal least-squares procedure. The positions of all the 14 hydrogen atoms in the phenyl rings were deduced from a difference Fourier map, but both hydrogen atoms in the methylene group were located geometrically. The R value was reduced to 0.091 for 1741 observable reflections by blockdiagonal least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the hydrogen atoms. The atomic coordinates are listed in Table 2. The atomic scattering factors for Cl, N, and C were those of the International Tables for X-Ray Crystallography.[7] For the hydrogen atom, the scattering factor was adopted from the table of Stewart *et al.*[8]

Description of the Structure

The molecular structure of Cl-TPV and the numbering system are illustrated in Fig. 4. The bond

Table 2. Fractional atomic coordinates of Cl-TPV[a]

Atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$
C (1)	3709 (3)	95 (11)	2826 (3)
C (2)	2805 (3)	1300 (10)	2133 (3)
C (3)	4391 (3)	766 (10)	1901 (3)
C (4)	4875 (3)	−238 (11)	2168 (3)
C (5)	5441 (2)	−190 (10)	1878 (3)
C (6)	5533 (2)	827 (10)	1331 (3)
C (7)	5049 (3)	1822 (12)	1075 (3)
C (8)	4479 (3)	1790 (11)	1354 (3)
C (9)	3293 (2)	2100 (10)	3694 (2)
C (10)	2920 (3)	3507 (11)	3868 (3)
C (11)	2967 (3)	4291 (12)	4455 (3)
C (12)	3397 (3)	3633 (12)	4888 (3)
C (13)	3754 (3)	2208 (12)	4716 (3)
C (14)	3714 (3)	1328 (10)	4122 (3)
C (15)	2245 (3)	1398 (10)	1753 (3)
C (16)	2264 (3)	1832 (11)	1123 (3)
C (17)	1742 (3)	1929 (12)	773 (3)
C (18)	1193 (3)	1600 (11)	1060 (3)
C (19)	1156 (3)	1149 (11)	1678 (3)
C (20)	1686 (3)	1014 (11)	2027 (3)
N (1)	3815 (2)	767 (8)	2188 (2)
N (2)	3326 (2)	1038 (8)	1824 (2)
N (3)	2745 (2)	1684 (8)	2749 (2)
N (4)	3265 (2)	1379 (8)	3082 (2)
Cl	520 (1)	1814 (3)	631 (1)

a) The coordinates of hydrogen atoms, the anisotropic and isotropic thermal parameters, and the $F_o - F_c$ table are kept by the office of the Chemical Society of Japan (Document No. 8145).

lengths and the bond angles are listed in Table 3. The four nitrogen atoms are coplanar (N-plane) within ±0.001 Å and the *sym*-tetrazinyl ring has a deformed boat form; these have been observed in other verdazyls.[9-11] The atomic deviations from N-plane are as follows: C(1)=0.62, C(2)=0.14, C(3)=−0.34, C(9)=−0.42, and C(15)=0.30 Å. These values are close to those of DTPV and TPV except that C(9) (−0.22 Å in TPV). The dihedral angles between N-plane and each plane of N(1)-, N(4)- and C(2)-phenyl rings are 37.5, (−)35.7, and 25.5°, respectively. The twist angles around the inter-ring bonds, defined by the dihedral angle between the plane of each phenyl ring and the plane through α-, β-, γ-, and γ'-atoms, are 20.9, (−)15.6, and 25.2° for N(1)–C(3), N(4)–C(9), and C(2)–C(15) bonds, respectively. The last angle is much greater than those in the other verdazyls examined, this fact is attributed to the intermolecular packing forces, as can be seen from Fig. 5.

Table 3. Bond lengths (l/Å) and bond angles (ϕ/°)
The estimated standard deviations are less than 0.01 Å and 1°, respectively.

Bond	Length	Bond	Length
C(1)-N(1)	1.47	C(9)-N(4)	1.41
C(1)-N(4)	1.44	C(10)-C(11)	1.38
C(2)-C(15)	1.48	C(11)-C(12)	1.40
C(2)-N(2)	1.34	C(12)-C(13)	1.35
C(2)-N(3)	1.35	C(13)-C(14)	1.42
C(3)-C(4)	1.40	C(15)-C(16)	1.38
C(3)-C(8)	1.40	C(15)-C(20)	1.39
C(3)-N(1)	1.41	C(16)-C(17)	1.37
C(4)-C(5)	1.39	C(17)-C(18)	1.38
C(5)-C(6)	1.38	C(18)-C(19)	1.36
C(6)-C(7)	1.40	C(19)-C(20)	1.39
C(7)-C(8)	1.39	N(1)-N(2)	1.34
C(9)-C(10)	1.35	N(3)-N(4)	1.37
C(9)-C(14)	1.42	C(18)-Cl	1.75

Bond	Angle	Bond	Angle
N(1)-C(1)-N(4)	105	N(4)-C(9)-C(14)	119
C(1)-N(1)-N(2)	117	C(14)-C(9)-C(10)	121
N(1)-N(2)-C(2)	115	C(9)-C(10)-C(11)	121
N(2)-C(2)-N(3)	126	C(10)-C(11)-C(12)	121
C(2)-N(3)-N(4)	113	C(11)-C(12)-C(13)	118
N(3)-N(4)-C(1)	118	C(12)-C(13)-C(14)	123
C(1)-N(1)-C(3)	123	C(13)-C(14)-C(9)	117
N(2)-N(1)-C(3)	118	N(2)-C(2)-C(15)	117
N(1)-C(3)-C(4)	121	N(3)-C(2)-C(15)	116
N(1)-C(3)-C(8)	119	C(2)-C(15)-C(16)	122
C(8)-C(3)-C(4)	120	C(2)-C(15)-C(20)	120
C(3)-C(4)-C(5)	119	C(20)-C(15)-C(16)	119
C(4)-C(5)-C(6)	122	C(15)-C(16)-C(17)	121
C(5)-C(6)-C(7)	119	C(16)-C(17)-C(18)	119
C(6)-C(7)-C(8)	121	C(17)-C(18)-C(19)	122
C(7)-C(8)-C(3)	120	C(18)-C(19)-C(20)	119
C(1)-N(4)-C(9)	124	C(19)-C(20)-C(15)	120
N(3)-N(4)-C(9)	117	C(17)-C(18)-Cl	120
N(4)-C(9)-C(10)	120	C(19)-C(18)-Cl	119

Figure 5 shows how the Cl-TPV molecules are arranged in the unit cell. The molecules form columns along the b axis. The shortest intermolecular distance between the non-hydrogen atoms is 3.48 Å for the N(1)···C(19) contact in the column. This columnar structure seems very similar to that of DTPV, as can be seen from Fig. 6.[11] Within the column, the mean values of the intermolecular distances for the π-framework are actually 7.05 and 7.15 Å for Cl-TPV and DTPV, respectively, while they are 7.76—7.86 Å for the other verdazyls. However, there are some substantial differences between Cl-TPV and

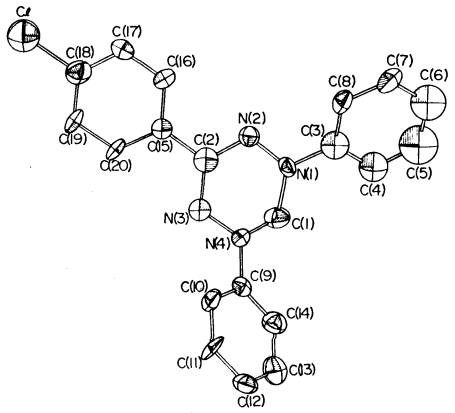

Fig. 4. Molecular structure of Cl-TPV and the numbering system.

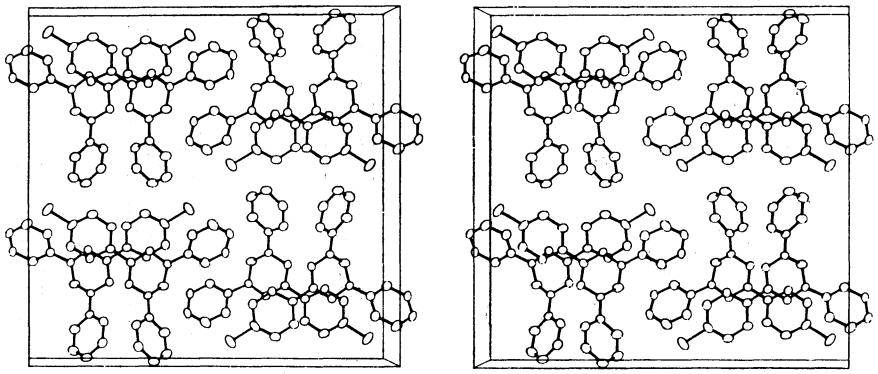

Fig. 5. Stereoscopic view of the crystal structure of Cl-TPV along the b axis. The a axis is horizontal, from left to right, and the c axis is downward vertical. The hydrogen atoms were omitted for clarity.

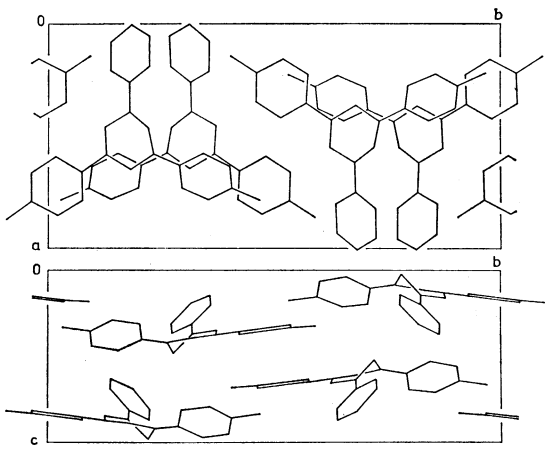

Fig. 6. Molecular packing of DTPV.[11]
The methyl carbon atom in C-tolyl group makes the outmost thorn of the column along the c axis.

DTPV, *e.g.* in the shortest N···N contact: 3.74 Å in the former, but 4.15 Å in the latter.

Discussion

The susceptibilities of a number of verdazyls have been described by the Heisenberg linear chain model.[2,12,13] The numerical study of the thermodynamic properties of the Heisenberg linear chain of $S=1/2$ spins has been made by Bonner and Fisher.[14] The theory predicts the following relation independent of the exchange parameter, J:

$$\chi_{max}T_{max} = 0.142. \quad (1)$$

The predicted susceptibility for antiferromagnetic coupling exhibits a round maximum at

$$T_{max} = 1.282|J|/k, \quad (2)$$

where k is the Boltzmann constant. The susceptibility of Cl-TPV gives 0.141 for Relation (1). Based on Eq. 2, the exchange parameter is estimated to be $J/k=-16.4$ K; this is the strongest antiferromagnetic exchange interaction among the verdazyl mono-radicals examined. The solid line in Fig. 2 is the susceptibility of the Heisenberg linear chain with this J value. The calculated susceptibility is very close to the observed one. The systematic disagreement in the lowest temperature region can be attributed to a small amount of impurities; it is hard to prepare and keep the radical completely pure. Therefore, an adequate model to describe the susceptibility of the Cl-TPV crystal is the Heisenberg linear chain model with $J/k=-16.4$ K.

Because the exchange interaction between the aromatic radicals is caused by the overlapping between the p_z π-orbitals, the Cl-TPV molecules in the column are coupled to one another by the exchange interaction. Therefore, a Cl-TPV crystal is a one-dimensional magnet in view of the molecular packing. This is consistent with the result derived from the susceptibility.

An approximated spin density Hamiltonian for the exchange interaction between the aromatic radicals A and B has been presented by McConnell:[15]

$$\mathscr{H}^{AB} = -\boldsymbol{S}^{A}\boldsymbol{S}^{B}\sum J_{ij}^{AB}\rho_i^A\rho_j^B, \quad (3)$$

where $\boldsymbol{S}^A$ and $\boldsymbol{S}^B$ are the total spin operators on molecules A and B, ρ_i^A and ρ_j^B are the π-spin densities on atoms i and j of A and B, respectively, and where J_{ij}^{AB} is the two-center exchange integral between i and j. The observed J corresponds to the summation in Eq. 3. Using this equation the ferromagnetic exchange interaction in a galvinoxyl radical crystal has been discussed.[16] The same procedure has been applied to TPV and its methyl derivatives.[2] According to that study, the order of the observed J's can be explained by means of the following tractable function for J_{ij}^{AB}:

$$J_{ij}^{AB} = -pC/r_{ij}^{AB}, \quad (4)$$

where C is a positive constant, r_{ij}^{AB} is the distance between atoms i and j, and where p is an angular correction. A possible angular correction is $p=\cos\theta_i^A\cos\theta_j^B$ where θ_i^A and θ_j^B are the angles between respective axes of the $p_z\pi$-orbitals of i and j atoms j and the vector distance $\boldsymbol{r}_{ij}^{AB}$.[17] However, the following rather crude correction factor was adopted:

$$p = \begin{cases} 1 & \text{when } r_{ij}^{AB} \leqq 6\text{ Å} \\ 0 & \text{when } r_{ij}^{AB} > 6\text{ Å}. \end{cases} \quad (5)$$

When the layered structure with the separation of 4 Å between the layers is assumed,

$$\left.\begin{array}{l} r_{ij}^{AB} \leqq 6\text{ Å corresponds to } \cos\theta_i^A\cos\theta_j^B \geqq 0.45 \\ \text{and} \\ r_{ij}^{AB} > 6\text{ Å corresponds to } \cos\theta_i^A\cos\theta_j^B < 0.45. \end{array}\right\} \quad (6)$$

When other functions for J_{ij}^{AB}, such as the overlap integral and exchange integral calculated by Dulčić and Herak,[18] were adopted, the order of the observed J's has been reversed.[2]

The spin densities on Cl-TPV are similar to those on TPV, in view of the same hyperfine coupling constant due to nitrogen nuclei. The same spin distribution as that of Cl-TPV can be reasonably assumed for DTPV. Therefore, the spin densities for Cl-TPV and DTPV used in the calculation are taken to be identical with those for TPV discussed elsewhere;[16] they are shown in Table 4.

Using Eqs. 4 and 5, the summation in Eq. 3 has been calculated for pairs of molecules along the three crystallographic axes. The results are summarized in Table 5, together with those for DTPV. The prominent negative value suggests the antiferromagnetic

Table 4. The π-spin density distribution in Cl-TPV

Atom	Spin density
N (1), N (4)	0.2040
N (2), N (3)	0.1944
C (2)	−0.0461
C (3), C (9)	−0.0345
C (4), C (8), C (10), C (14)	0.0473
C (5), C (7), C (11), C (13)	−0.0179
C (6), C (12)	0.0505
C (15)	0.0032
C (16), C (20)	−0.0179
C (17), C (19)	0.0067
C (18)	−0.0131

Table 5. Results of the calculation based on McConnell's spin density Hamiltonian

Direction in the crystal	Sum in Eq. 3[a]	
	Cl-TPV	DTPV[2]
Along the a axis	−3.41	
Along the b axis	−16.4	
along c axis		−21.3
Along the c axis	0.0369	
Observed J/k	−16.4 K	−11.1 K

a) The sums have been adjusted by using the factor obtained from the observed J for Cl-TPV and the calculated J along the b axis of the Cl-TPV crystal.

exchange coupling in the column along the b axis of the Cl-TPV crystal. The calculated exchange couplings between the columns are less than 1/5 of that within the column. These results are consistent with the fact derived from the susceptibility: an antiferromagnetic linear chain spin system. The ratio of the observed J of Cl-TPV to that of DTPV is 1.5. However, the calculated ratio is 0.8; this is not improved by adopting the squared cosine factor for p. The three other functions for J_{ij}^{AB} in Ref. 2 give the ratios of 0.7—0.004, where 0.7 is obtained with $J_{ij}^{AB}=-pC(r_{ij}^{AB})^{-3}$. In conclusion, Eq. 3 combined with Eqs. 4 and 5 has roughly explained the order of the observed J's of five verdazyl radicals. This tractable procedure would thus be practically more useful in correlating the exchange interaction with the crystal structure than complicated procedures, such as that adopted by Dulčić and Herak.[18]

The authors wish to thank Professors Yasuo Deguchi, Hiroaki Ohya-Nishiguchi, Noboru Hirota, and Masayoshi Kinoshita for their helpful discussions.

References

1) "The Magnetic Properties of Verdazyl Free Radicals," part XIII.
2) N. Azuma, in preparation.
3) P. H. H. Fischer, *Tetrahedron*, **23**, 1939 (1967).
4) C. Schiele, K. Halfar, and G. Arnold, *Z. Naturforsch.*, **226**, 105 (1967).
5) M. Mekata, *J. Phys. Soc. Jpn.*, **17**, 796 (1962).
6) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956).
7) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.
8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
9) D. E. Williams, *Acta Crystallogr., Sect. B*, **29**, 96 (1973).
10) N. Azuma, Y. Deguchi, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **48**, 819, 825 (1975).
11) N. Azuma, *Bull. Chem. Soc. Jpn.*, **53**, 2671 (1980).
12) K. Mukai, K. Oishi, K. Ishizu, and N. Azuma, *Chem. Phys. Lett.*, **23**, 522 (1973).
13) N. Azuma, K. Ishizu, and K. Mukai, *J. Chem. Phys.*, **61**, 2294 (1974).
14) J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, **135**, 640 (1964).
15) H. M. McConnell, *J. Chem. Phys.*, **39**, 1910 (1963).
16) N. Azuma, J. Yamauchi, K. Mukai. H. Ohya-Nishiguchi, and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **46**, 2728 (1973).
17) W. Duffy, Jr., D. L. Strandburg, and J. F. Deck, *J. Chem. Phys.*, **68**, 2097 (1978).
18) A. Dulčić and J. N. Herak, *Mol. Phys.*, **26**, 605 (1973).