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Ab initio Study of the Relationship between the Pressure and the Change in the Dipole Moment of a Molecule in a Ferroelectric Crystal[#]

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(Received May 19, 1993)

The typical properties of a ferroelectric material are piezoelectricity and pyroelectricity. In this study we considered in detail the relationship between the pressure and the change in the dipole moment of a molecule in a ferroelectric crystal from the standpoint of piezoelectricity. We applied *ab initio* molecular orbital calculations involving the crystal effect to the orthorhombic thiourea ($(NH_2)_2CS$) crystal model as the ferroelectric crystal model. The molecular structure obtained by this calculation was in fairly good agreement with the result obtained by X-ray analysis. In order to investigate the substituent effects, we calculated a hypothetical orthorhombic N,N'-difluorothiourea ($(NHF)_2CS$) crystal model in a similar manner.

One of the typical properties of a ferroelectric material is piezoelectricity. In order to investigate piezoelectricity, we calculated the pressure dependence of the structure and the dipole moment of a molecule in a ferroelectric crystal.

In general, it is difficult to apply the *ab initio* method to ferroelectric crystals, because many ferroelectric materials contain a transition metal and the structure is complicated. We therefore applied the *ab initio* method to the thiourea ($(NH_2)_2CS$) crystal model. Thiourea doesn't contain a transition metal and the structure is relatively simple.

Thiourea is a planar molecule and the ferroelectricity in this crystal has been reported by Solomon in 1956.[1)] An analysis of the low-temperature structure and a dielectric measurement were carried out by White and Goldsmith.[2)] They classified the thiourea crystal in terms of the value of the dielectric constant into five phases. Phase I (below −105 °C) and phase III (between −97 and −94 °C) are ferroelectric phases. Subsequently, the crystal structure and ferroelectricity for thiourea have been studied extensively by many investigators,[3—7)] and it has become apparent that the crystal has the orthorhombic form in phase I.

In this study we applied *ab initio* molecular orbital calculations involving crystal effects in order to study the relationship between the pressure and the change in the dipole moment of the molecule in an orthorhombic thiourea crystal, as the first step to investigate the mechanism for the appearance of piezoelectricity. We then calculated the hypothetical orthorhombic N,N'-difluorothiourea ($(NHF)_2CS$) crystal model in a similar manner as in the study of usual substituent effects.

Method of Calculations

1. Structural-SCF Method (S-SCF method). It is difficult to obtain the electronic structure of a molecule in a crystal at the *ab initio* level, because such calculations require a large crystal model to involve the crystal effect. Therefore, in order to treat the crystal effect efficiently, we used the method described below.

An outline of our method is schematically shown in Fig. 1. Molecules in the crystal are separated into environmental molecules (E) and a central molecule (C), as in a previous paper.[8)] At first, we optimize the structure of the central molecule while fixing the structure of environmental molecules. The optimized structure of the central molecule (C′) is thus determined involving the effect of the interaction with the environmental molecule (I). Next, the structure of the environmental molecules is replaced by the optimized structure of the central molecule. In this case, the position of the central atom of the environmental molecule, say, carbonyl carbon, is fixed. We then optimize the structure of the central molecule under the influence of the potential by the environmental molecules with the replaced geometry (II). These procedures are carried out repeatedly until the optimized structure of the central molecules is consistent with the fixed structure of environmental molecules; this converged structure (E_C, C_C) is regarded as being the optimized structure with the crystal effect (III). This method is hereafter referred to as the structural-SCF (S-SCF) method. In the present calculations, the number of environmental molecules was 4, as is shown in Fig. 3. The number of the iterations for the geometry optimization was usually between 2 and 5.

By using the S-SCF method, we can calculate the electronic structure of a relatively large molecule in a crystal at the *ab initio* level. Since this method is simply a series of repetitions of usual *ab initio* SCF calculations, we can use the available program packages for molecular orbital cal-

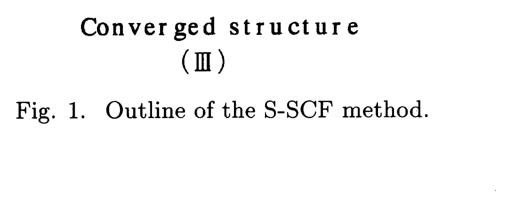


Fig. 1. Outline of the S-SCF method.

[#] This paper is dedicated to late Professor Hiroshi Kato.

culations without any modifications. In practice, we used GAUSSIAN 88[9)] and GAUSSIAN 90.[10)] These calculations were carried out with the 3-21G* basis set in order to take into account the polarization functions for the sulfur atom.

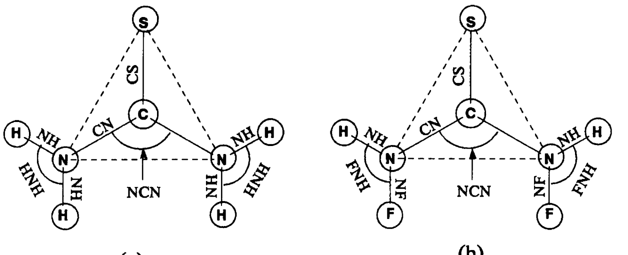
2. Orthorhombic Thiourea Crystal Model. We show the parameters used to determine the molecular structure for thiourea and *N*,*N'*-difluorothiourea in Fig. 2. These molecules have an advantage in that we can understand the relationship between the structure and the dipole moment easily, because the molecular framework is the trigonal form, as is shown by the dotted line in Fig. 2.

A simplified orthorhombic crystal model for these compounds is shown in Fig. 3. This crystal model comprises one central molecule and four environmental molecules. In this study, in order to study the change in the structure and the dipole moment with the pressure from the *a*-axis direction in Fig. 3, the molecules in the crystal model were arranged so as to be parallel to each other. Therefore, great changes in the crystal structure, such as the rotation of the molecules, were not the target of the present research.

R_1, R_2, and R_3 in Fig. 3 denote the intermolecular distances. Thus, the crystal structure is determined by these parameters. R_2 is half of the distance between two environmental molecules in the same plane and R_3 is the deviation from central molecule to the environmental molecules. R_1 is the distance between the central molecule and the environmental molecules along the *a*-axis. First of all, R_1, R_2, and R_3 were optimized using the S-SCF method described in the previous paragraph. Next, we changed the value of R_1 from its optimized value by a constant value, ΔR_1. With the newly fixed value of R_1, S-SCF calculations were performed until the newly optimized geometry of the molecules in question was obtained. Then, the energy difference (ΔE) from the optimized value was obtained. We calculated the quantity P as follows:

$$P = \frac{\left(\frac{\Delta E}{\Delta R_1}\right)}{A} \times 4.3024 \times 10^7 (\text{atm}), \qquad (1)$$

where ΔE is represented in a.u. and ΔR_1 in Å. The quantity P can reasonably be considered to be a measure of the pressure. Therefore, this quantity is hereafter tentatively referred to as the pressure. A is the area in which the pressure is applied, and is shown in Fig. 3. A is represented in units of $(\text{Å})^2$. Consequently, we can regard R_1 as being a parameter for the pressure. Strictly speaking, the pressure (P) isn't what we called the pressure, itself, because the total energy of the crystal should be calculated under the periodic boundary condition, while only the total energy of a cluster was calculated in the present study. However, we can regard this value as being a reference pressure in order to compare the calculated value for thiourea to that for *N*,*N'*-difluorothiourea.



(a) (b)

Fig. 2. Parameters used to determine the molecular structure for thiourea (a) and *N*,*N'*-difluorothiourea (b). The dotted line shows the framework of molecule.

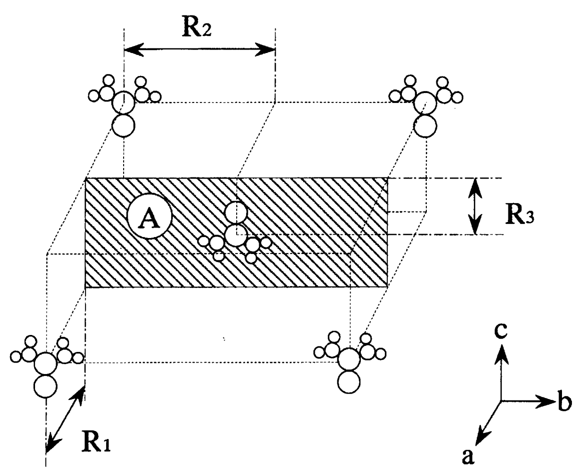


Fig. 3. Simplified orthorhombic crystal model. The R_1, R_2, and R_3 show the parameters used to determine the crystal structure. The slant line shows the area (A) in which the pressure is applied.

Results and Discussion

1. Molecular Structure and Dipole Moment under 1 Atmosphere. In order to obtain the molecular structure in a crystal and the lattice constants of the crystal, we applied the S-SCF method to the crystal model of thiourea and *N*,*N'*-difluorothiourea. All of the parameters for the molecular and crystal structure were optimized in these calculations. For a comparison, we calculated the optimized structure of a single molecule with the 3-21G* and 6-31G** basis set. Table 1 indicates the results of an X-ray analysis at −103 °C, carried out by Tanisaki et al.,[3)] together with the calculated results for an isolated thiourea.

The results of the S-SCF method are in better agreement with the experimental results than that by calculations of the optimized structure for a single molecule with both basis sets. Therefore, the S-SCF method can reasonable be considered to include the crystal effect. However, we didn't obtain a good agreement for the N–H bonds. It is well known that there is an uncertainty with regard to the position of the hydrogen atom, which is a disadvantage of the X-ray analysis. As a whole, the geometry obtained by the S-SCF method is in excellent agreement with the experimental results. We may thus expect a similar agreement for *N*,*N'*-difluorothiourea.

We then calculated the dipole moment of a single molecule, while fixing the geometry optimized by the S-SCF method with the 6-31G (3D) basis set. The dipole moments of thiourea and *N*,*N'*-difluorothiourea were calculated to be 6.40 debye (1 debye=3.3356×10^{-3}

Table 1. Optimized Structure of the Crystal and Molecule for Thiourea and *N*,*N*′-Difluorothiourea at 1 atm Obtained by the S-SCF Calculation

The results of the optimized structure of isolated molecule and X-ray diffraction method for thiourea. All lengths and angles are in Å and degree, respectively.

	R_1	R_2	R_3	C–S	C–N	N–H		N–C–N	H–N–H	F–N–H
$(NH_2)_2CS$										
S-SCF										
3-21G*	2.1321	2.9931	1.0568	1.7230	1.3283	0.9997	0.9997	117.688	116.368	—
EXP.[a)]				1.721	1.322	0.83 0.86	0.97 0.91	118.6	117 120	—
3-21G* [b)]				1.6842	1.3423	0.9969	0.9969	115.937	118.505	—
6-31G** [b)]				1.6833	1.3365	0.9923	0.9923	115.740	118.940	—
$(NHF)_2CS$										
S-SCF										
3-21G*	2.1866	2.9595	0.6882	1.7247	1.3217	1.0011	1.3980 (N–F)	121.245	—	111.596

a) Ref. 3. b) Optimized structure of an isolated molecule.

C m) and 1.88 debye, respectively. We regard these values of the parameters for the crystal structure, molecular structure and the dipole moment as being reference values at 1 atm.

2. Molecular Structure and Dipole Moment under High Pressure. We decreased the value of R_1 from the optimized values (reference value) to 1.7321 Å for thiourea and 1.7866 Å for *N*,*N*′-difluorothiourea, respectively; that is, we decreased R_1 by 0.1 Å, and optimized the molecular structure as well as R_2 and R_3 for each value of R_1 with the 3-21G* basis set. The dipole moment of the molecule with the optimized structure for each value of R_1 was calculated for a single molecule with 6-31G(3D). Further, in order to investigate the dependence of the dipole moment on the bond length or bond angle, we calculated the dipole moments for a single molecule with the optimized structure at 1 atm.

We calculated the pressure for each value of R_1 from the energy change with ΔR_1 and using the previously-mentioned area (A). The value of A was determined by using the van der Waals radius and the covalent bond length. The values of A for thiourea and *N*,*N*′-difluorothiourea were calculated to be 96.4008 $(\text{Å})^2$ and 104.4574 $(\text{Å})^2$, respectively. After all, the range of the pressure was obtained to be about from 2.0×10^3 to 25×10^3 atm for thiourea and about from 2.0×10^3 to 15×10^3 atm for *N*,*N*′-difluorothiourea.

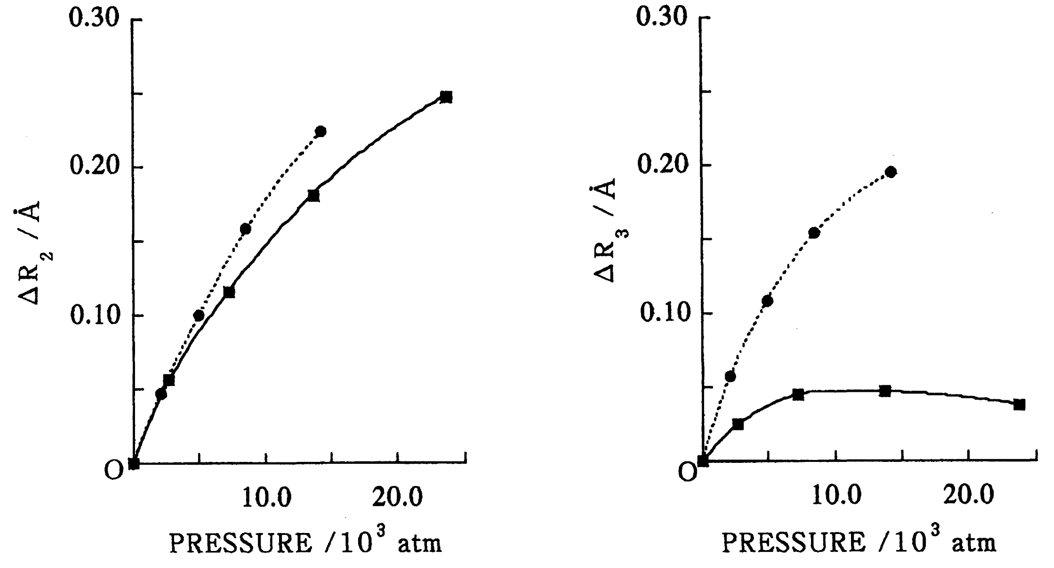
These results are given in Figs. 4, 5, 6, and 7, in which only the differences from the reference values are indicated. The dependence of the change in the crystal structure upon the pressure is shown in Fig. 4. The change in the value of R_3 for *N*,*N*′-difluorothiourea is much greater than that for thiourea, while the value of R_2 changes similarly for both molecules. It seems that the difference in the change of R_3 is cause by the difference in the steric hindrances; that is, the steric hindrance between sulfur and hydrogen for thiourea and that between sulfur and fluorine for *N*,*N*′-difluorothiourea.

Figures 5 and 6 show the pressure dependence of the bond length and the bond angle, respectively. The most sensitive bond for the pressure is the C–S bond, followed by the C–N bond for both molecules. For the bond angle, a similar tendency of the pressure dependence was found, as shown in Fig. 6. On the whole, *N*,*N*′-difluorothiourea has a larger pressure dependence than does thiourea.

Next, we calculated the change in the dipole moment when only the bond lengths were changed while fixing all bond angles under an applied pressure (hereafter, referred to as $\Delta\mu_{\text{Leng.}}$). Similarly, $\Delta\mu_{\text{Ang.}}$ was calculated for the bond angle.

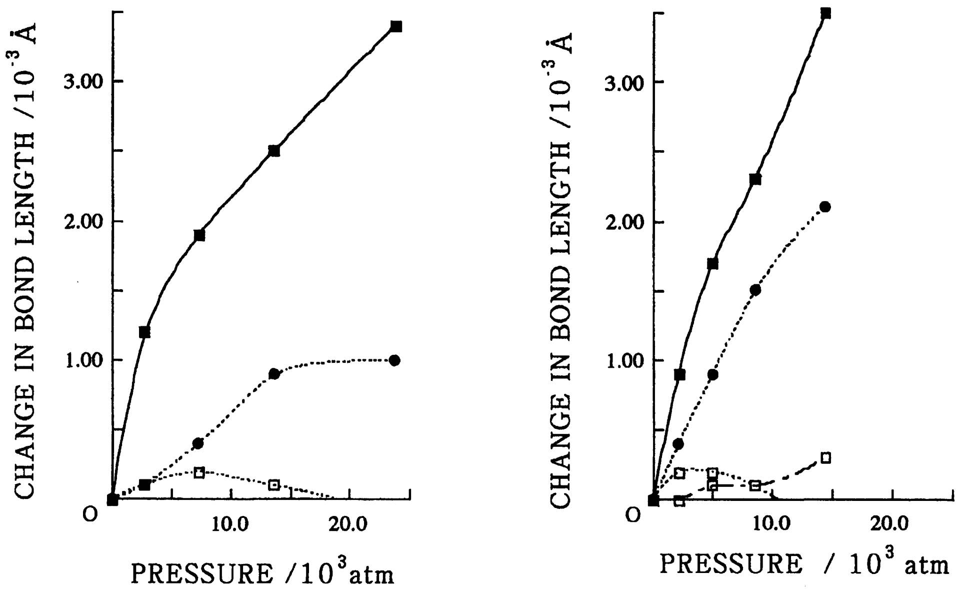
We denote $\Delta\mu_{\text{Leng.+Ang.}}$ as the sum of the bond-length dependence of the change in the dipole moment ($\Delta\mu_{\text{Leng.}}$) and the bond-angle dependence one ($\Delta\mu_{\text{Ang.}}$), in order to study the additivity of the dipole moment. The pressure dependence of the dipole moment is shown in Fig. 7.

The thus-obtained value of $\Delta\mu_{\text{Leng.+Ang.}}$ was compared with the dipole moment of those molecules with an optimized geometry (hereafter referred to as $\Delta\mu_{\text{Full}}$). Since $\Delta\mu_{\text{Leng.+Ang.}}$ is in complete agreement with the dipole moment of the optimized structure ($\Delta\mu_{\text{Full}}$), as shown in Fig. 7, it is obvious that the additivity is retained for the dipole moment contributions of $\Delta\mu_{\text{Leng.}}$ and $\Delta\mu_{\text{Ang.}}$. We obtained the reverse tendency between thiourea and *N*,*N*′-difluorothiourea concerning the magnitude of $\Delta\mu_{\text{Leng.}}$ and $\Delta\mu_{\text{Ang.}}$; that is, the dependence of the dipole moment on the bond length is dominant for thiourea, while the dependence of the dipole moment on the bond angle is dominant for *N*,*N*′-difluorothiourea. In order to analyze this result, we must obtain detailed knowledge concerning the change in the dipole moment. Consequently, the relationship between the molecular structure and the dipole moment



(a) (b)

Fig. 4. Pressure dependence of the intermolecular distances (ΔR_2 (a) and ΔR_3 (b)) for thiourea (■) and *N*,*N*′-difluorothiourea (●).



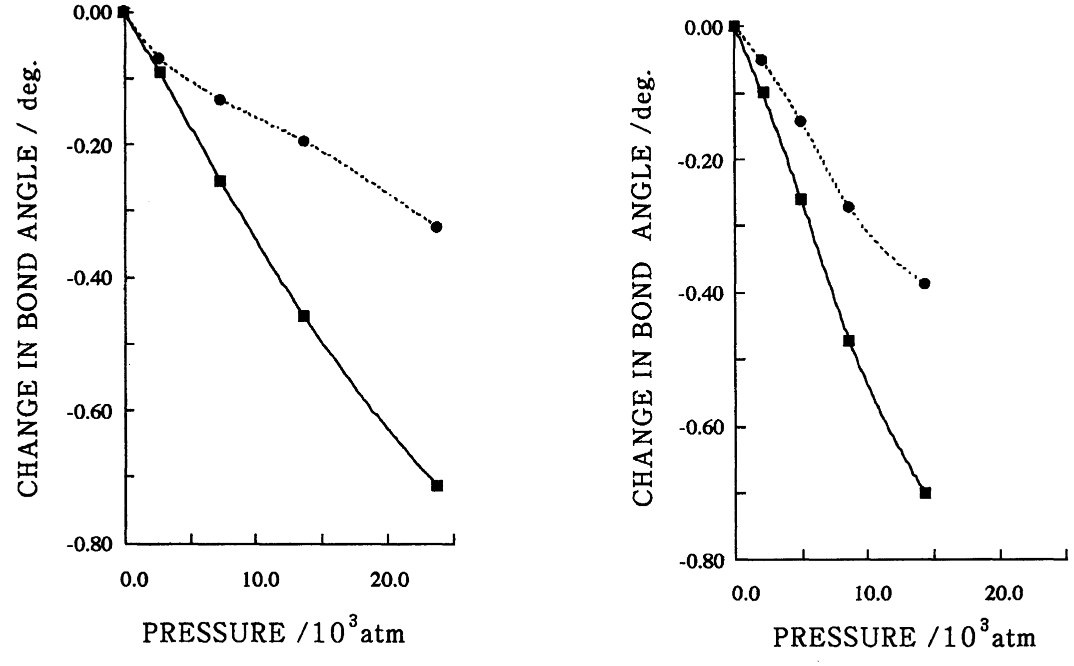
(a) (b)

Fig. 5. Pressure dependence of the bond lengths for thiourea (a) and *N*,*N*′-difluorothiourea (b): -■-, C–S; ·●·, C–N; ·□·, N–H; -□-, N–F.

is discussed in the following section.

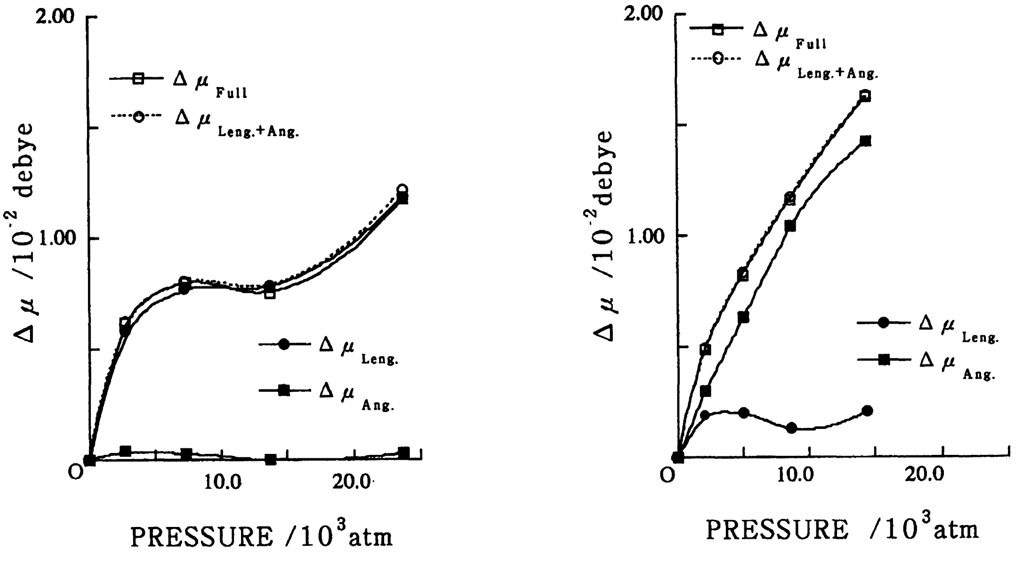
3. Dependences of the Dipole Moment of Each Bond Length and on Each Bond Angle. By applying pressure, each bond length and each bond angle should change to some extent, resulting in a change in the dipole moment. For an analysis, we changed only a specified bond length to the optimized value, while fixing the other bond lengths and all bond angles at values under 1 atm, and calculated the dipole moment. Next, a specified bond angle was varied while fixing the other bond angles and all of the bond lengths. The calculated values are shown in Figs. 8 and 9. All of the values of each term in Figs. 8 and 9 are summed up in order to consider whether the additivity of the dipole moment holds or not. Here, the sum of each term is denoted as $\Delta\mu_{\mathrm{Add.}}$ in Figs. 8 and 9.

Obviously the additivity of the dipole moment holds for both molecules. Consequently, we expect to be able to analyze the relationship between the molecular structure and the pressure dependence of the dipole moment



(a) (b)

Fig. 6. Pressure dependence of the bond angles for thiourea (a) and *N*,*N*′-difluorothiourea (b): -■-, N–C–N; ·●·, H–N–H or F–N–H.

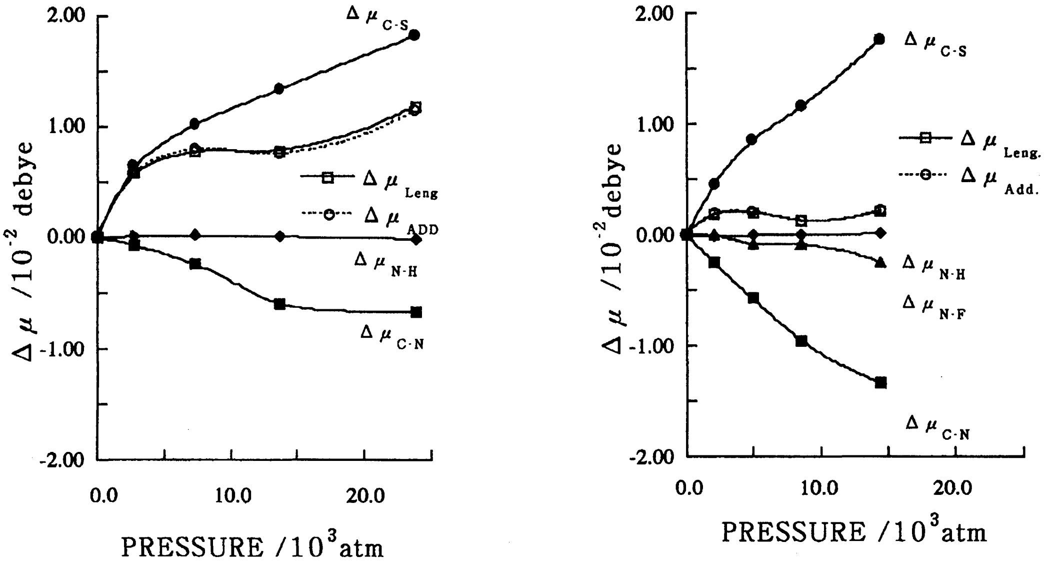


(a) (b)

Fig. 7. Pressure dependence of the change in the dipole moment ($\Delta\mu$), the pressure dependence of the change in the dipole moment accompanied by variation of the bond lengths only and the bond angles only ($\Delta\mu_{\mathrm{Leng.}}$ and $\Delta\mu_{\mathrm{Ang.}}$) and the sum of $\Delta\mu_{\mathrm{Leng.}}$ and $\Delta\mu_{\mathrm{Ang.}}$ ($\Delta\mu_{\mathrm{Leng.+Ang.}}$) for thiourea (a) and *N*,*N*′-difluorothiourea (b).

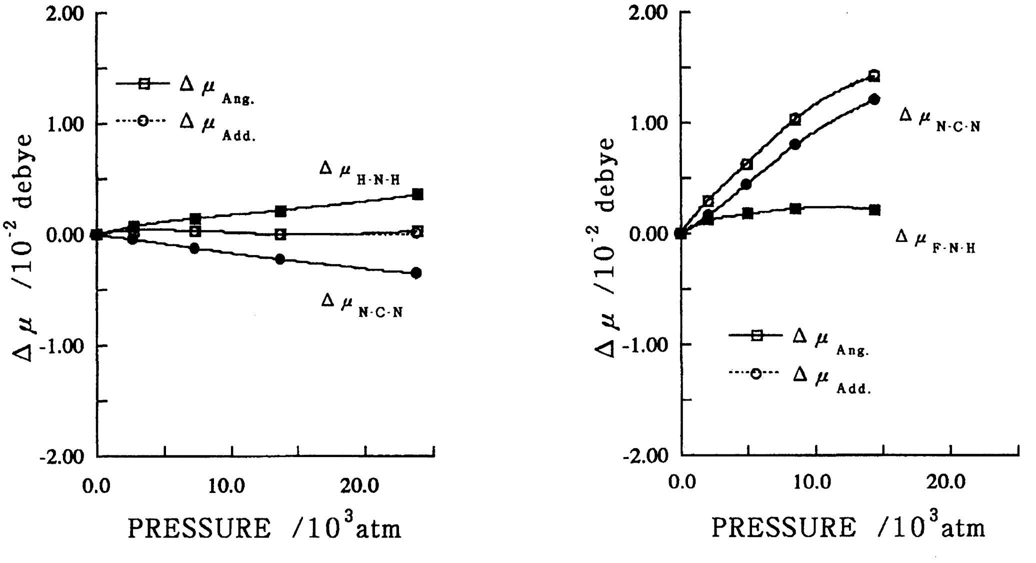
in terms of the bond dipole moment.

We then defined the dipole moment of each bond or bond angle as μ^{p}; superscript p indicates the name of the bond, that is, μ^{p} was calculated by employing the Mulliken total atomic charges in order to analyze the dipole moment of the molecule. It should be noted that μ^{p} is represented by the product of the bond length and the charge. The Mulliken total atomic charges are shown in Fig. 10; the arrow line indicates the direction of μ^{p} in this figure. It should be pointed out that since the $\mu_x{}^{\mathrm{p}}$, x component of μ^{p} vanishes because of the molecular symmetry, we consider only the y component



(a) (b)

Fig. 8. Pressure dependence of the change in the dipole moment accompanied by a variation in a specified bond length.

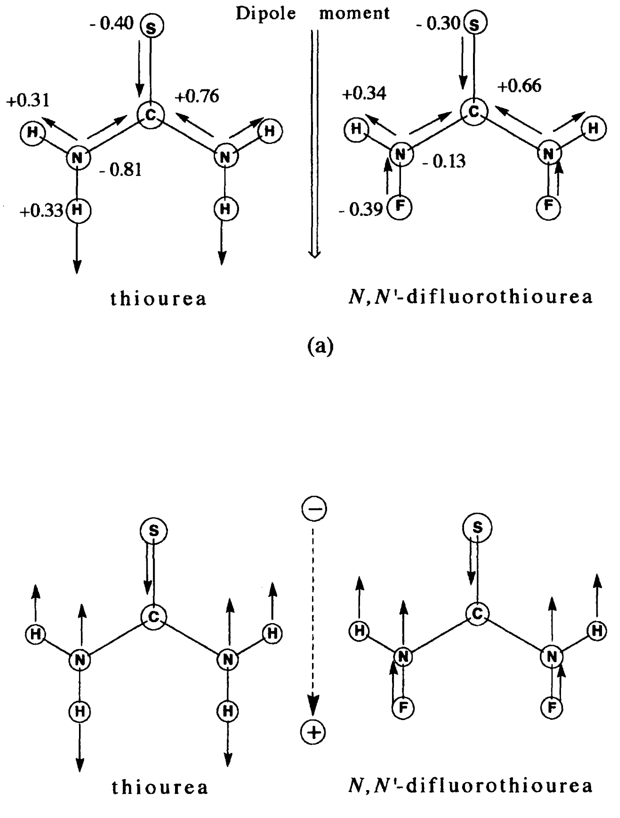


(a) (b)

Fig. 9. Pressure dependence of the change in the dipole moment accompanied by a variation in a specified bond angle.

$(\mu_y{}^{\mathrm{P}})$, represented hereafter by simply μ^{P} for the sake of brevity. We regard μ^{P} as being the contribution of each bond or bond angle to the dipole moment.

First, it is obvious from Fig. 10 that μ^{CS} and μ^{NH} have a positive contribution on the total dipole moment; μ^{CN} and μ^{NF} have a negative contribution. Second, Fig. 5 indicates that the C–N bond length remains approximately constant over the 15×10^3 atm for thiourea, and that the change in the C–N bond length is nearly linearly dependent upon an applied pressure for *N*,*N*′-difluorothiourea; similar changes are found for other structural parameters in both molecules, that is, the C–S bond length changes remarkable and the N–H or the N–F bond length changes only slightly. From these results we can easily explain the difference in the dipole moment dependences on the bond length for both molecules. That is to say, the dominant factor for thiourea is $\Delta\mu_{\mathrm{Leng.}}$, because the change in μ^{CN} is smaller than that of μ^{CS}, due to the small change in the C–N bond length under high pressure. On the other hand, $\Delta\mu_{\mathrm{Leng.}}$ for *N*,*N*′-difluorothiourea is not the dominant factor, since the magnitude of μ^{CN} is nearly as large as



(a)

(b)

Fig. 10. (a) Results of the Mulliken total atomic charge for thiourea and N,N'-difluorothiourea: →, the direction of μ^{P}; ⇒, the direction of dipole moment. (b) The y component of μ^{P} ($\mu_y{}^{\mathrm{P}}$) for thiourea and N,N'-difluorothiourea: →, the direction of $\mu_y{}^{\mathrm{P}}$.

that of μ^{CS} and their directions are opposite. That is, both the C–N and C–S bond length changes with increasing the pressure, as shown in Fig. 5 (b); however, the contributions to the change in the dipole moment are canceled by each other because of the opposite directions of μ^{CN} and μ^{CS}. These results show that although the value of μ^{P} is only approximate, we can use these values of μ^{P} qualitatively to explain the pressure dependence of the total dipole moment easily.

We now consider the dependence of the change in the dipole moment on the bond angle. The result is shown in Fig. 9. Obviously, the additivity is retained and $\Delta\mu_{\mathrm{HNH}}$ and $\Delta\mu_{\mathrm{FNH}}$ have a positive contribution for both compounds; however, the $\Delta\mu_{\mathrm{NCN}}$'s for thiourea and for N,N'-difluorothiourea have negative and positive contributions, respectively. In a similar manner as in the case for the bond length, we can't explain the behavior of the change in $\Delta\mu_{\mathrm{NCN}}$. We therefore defined $\mu^{\mathrm{CN+NH}}$ and $\mu^{\mathrm{CN+NF}}$ as being the sum of μ^{CN} and μ^{NH}, and of μ^{CN} and μ^{NF}, respectively, in order to analyze the large effect of the $\Delta\mu_{\mathrm{NCN}}$, since the values of μ^{CN} and μ^{NH} or μ^{NF} should be intimately related to the change in the bond angle N–C–N. Fig. 10 shows that μ^{NH} has a positive contribution and that μ^{CN} and μ^{NF} have a negative contribution. We calculated the values of $\mu^{\mathrm{CN+NH}}$ and $\mu^{\mathrm{CN+NF}}$ at 1 atm as well as near to 14×10^3 atm when only has bond angles are changed, while fixing all of the bond lengths. The obtained results are listed in Table 2.

It is shown in Table 2 that $\mu^{\mathrm{CN+NH}}$ for thiourea has a positive contribution and that the $\mu^{\mathrm{CN+NF}}$ for N,N'-difluorothiourea has a negative contribution. From Fig. 6, it is expected that the main changes in the geometry of both molecules are the N–C–N bond angles with a variation of the pressure from 1 atm to 14×10^3 atm. Therefore, $\Delta\mu_{\mathrm{NCN}}$ for thiourea is reasonably expected to decrease, because of a decrease in $\mu^{\mathrm{CN+NH}}$ due to its positive contribution; for N,N'-difluorothiourea, however, $\Delta\mu_{\mathrm{NCN}}$ increases upon a decrease in $\mu^{\mathrm{CN+NF}}$, which results from its negative contribution. As a result, $\Delta\mu_{\mathrm{NCN}}$ for thiourea and N,N'-difluorothiourea are negative and positive contributions, respectively.

Thus, the dominant factor for N,N'-difluorothiourea is $\Delta\mu_{\mathrm{Ang.}}$ because of the sum of two positive contributions, $\Delta\mu_{\mathrm{NCN}}$ and $\Delta\mu_{\mathrm{FNH}}$. On the other hand, $\Delta\mu_{\mathrm{Ang.}}$ for thiourea is almost counteracted by the sum of the negative and positive contributions, that is $\Delta\mu_{\mathrm{NCN}}$ and $\Delta\mu_{\mathrm{HNH}}$.

It seems to be relatively complicated to apply μ^{P} to an analysis of the bond angle dependence of the dipole moment. The effect of a change in the bond length on the total dipole moment is involved in μ^{P}, because μ^{P} is equal to the product of the charge and the bond length. On the other hand, since the bond angle is related to the dipole moment through a trigonometric function, it is necessary to consider the effect of a particular bond and some neighboring bonds in connection with the bond angle.

Nevertheless, we succeeded to explain the dependence of the charge in the dipole moment based on the structure of a molecule in a crystal.

Table 2. Change in the Dependence of μ^{NH}, μ^{NF}, μ^{CN}, $\mu^{\mathrm{CN+NH}}$, and $\mu^{\mathrm{CN+NF}}$ on the Pressure, When Only the Bond Angles Are Changed

a) Thiourea

Pressure/atm	μ^{NH}	μ^{CN}	$\mu^{\mathrm{CN+NH}}$
1.0	0.30552	−0.12316	0.18236
14×10^3	0.30580	−0.12502	0.18078
Diff.[a]/10^{-3}	+0.28	−1.86	−1.58

b) N,N'-Difluorothiourea

Pressure/atm	μ^{NF}	μ^{CN}	$\mu^{\mathrm{CN+NF}}$
1.0	−0.54240	−0.11659	−0.65899
14×10^3	−0.54179	−0.11655	−0.65834
Diff./10^{-3}	+0.61	+0.004	+0.65

a) The Diff. shows the difference in each value, for thiourea (a) and N,N'-difluorothiourea (b).

Conclusion

The S-SCF method makes it possible to carry out *ab initio* molecular-orbital calculations involving the crystal effect. The molecular structure of thiourea at 1 atm obtained by this calculation was in fairly good agreement with the experimental data.

We obtained opposite results for thiourea and *N*,*N*′-difluorothiourea regarding the pressure dependence of the bond length and the bond angle, because of a substituent effect. In order to investigate this result in detail, we analyzed the pressure-dependence of the dipole moment based on the contributions of each bond and each bond angle.

In the future, we will apply these methods to the ferroelectric materials of polymers and investigate the mechanism for the appearance of piezoelectricity.

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