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Population Analysis of (*R*)-Thiazolidine-4-carboxylic Acid

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The structure of (*R*)-thiazolidine-4-carboxylic acid was refined at 111 and 293 K, respectively. Population analysis, which refines the population of the electrons in the molecule, was carried out, the result being compared with that of theoretical calculation.

In studies on structure by means of X-ray diffraction, the recent development of the diffractometer has afforded intensity data accurate enough for discussion of the distribution of the electron cloud. The population analysis[1] deals with the observed electron density distribution quantitatively. The number of electrons in each non-bonded and bonded orbital is derived from the refinement, from which bond orders and charge distribution of the molecule can be discussed.

(*R*)-Thiazolidine-4-carboxylic acid is an analogue of the proline and cysteine, and the structure was determined by Chacko.[2] In this paper, the structure of this molecule at both 293 and 111 K was refined by the population analysis method, the electronic structure being discussed in comparison with the theoretical one.

Experimental

Two sets of intensity data were measured at 293 and 111 K with a four circle diffractometer. Each set has 4 octants of the reciprocal space measured in 2θ-θ mode. The crystal data and experimental conditions are given in Tables 1 and 2, respectively. The crystal was treated with liquid nitrogen before the data collection in order to prevent from suffering of the extinction effect. The average structure amplitudes among the equivalent reflections in each set was used for further calculations. The estimated standard deviations, $\sigma(|F_o|)$ of the amplitudes are given by

$$\sigma(|F_o|) = \sqrt{\sum_i \sigma_i(|F_i|)^2/N},$$

where σ_i denotes the e.s.d. of *i*-th equivalent reflection.

Structure

The structure was determined independently with the program of automatic structure determination.[3] The conventional refinement of the structure was carried out by the full matrix least squares method, applying the following weighting scheme.

$$\text{wt} = c \text{ when } |F_o| = 0$$

$$\text{wt} = 1.0/(\sigma(|F_o|)^2 + a|F_o| + b|F_o|^2) \text{ when } |F_o| > 0$$

a, *b*, and *c* were adjusted in such a way that the differences between the calculated and observed structure amplitudes are uniform in any region of the reciprocal space. The absolute configuration of the molecule was also determined to be the *R*-configuration from the anomalous scattering of the sulfur atom (Table 3).

TABLE 1. CRYSTAL DATA

Space group	$P2_12_12_1$	
Z	4	
Lattice constant	293 K	111 K
a	9.929±0.002 Å	9.813±0.002 Å
b	9.936±0.002 Å	9.885±0.002 Å
c	5.664±0.001 Å	5.663±0.001 Å
d_{calcd} (g/cm^3)	1.58	1.61
d_{obsd} (g/cm^3)	1.57	
Linear absorption coefficient μ (cm^{-1})	4.947	4.855

TABLE 2. EXPERIMENTAL CONDITIONS

Crystal size	0.1×0.1×0.2 mm^3	0.2×0.2×0.4 mm^3
Source	Mo *Kα*	Mo *Kα*
Scan speed (2θ deg./min)	2	4
Background (s)	10	10
$2\theta_{\max}$ (deg.)	70	70
Monochromator	Graphite (0 0 2) plane	
Temperature	111±3 K	293±3 K

TABLE 3. DETERMINATION OF THE ABSOLUTE CONFIGURATION (293 K)

	R config.	*S* config.
f''	−0.16	+0.16
R (%)	3.95	4.06
R_w (%)	2.27	2.35

After the refinement with all reflections, the structure was refined using the higher order reflections only at 111 K ($\sin\theta/\lambda \geqq 0.65$, hereafter HOR) to reduce the effect of the bonding electrons. In comparison with the case of the low-temperature refinement based on all the reflections, all the positional parameters showed no significant shifts , the values of the temperature factors becoming smaller than those of all the reflections as expected (Table 5).

The bond lenghts and angles, shown in Fig. 1, are essentially the same as those reported by Chacko.

Difference Fourier Synthesis

The difference Fourier synthesis was carried out with the low and high temperature data phased by the

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Table 4. Atomic coordinates (e.s.d. in parentheses)

	x/*a*	*y*/*b*	*z*/*c*
(a) 293 K			
S	−0.17160 (6)	0.11728 (5)	0.10730 (11)
O_1	0.0093 (2)	0.3874 (2)	−0.2755 (3)
O_2	−0.1531 (2)	0.4960 (2)	−0.0683 (3)
N	−0.1200 (2)	0.3510 (2)	0.3193 (3)
C_1	−0.0590 (2)	0.4126 (2)	−0.0924 (4)
C_2	−0.0147 (2)	0.3329 (2)	0.1295 (4)
C_3	0.0008 (2)	0.1821 (2)	0.0864 (4)
C_4	−0.1947 (2)	0.2206 (2)	0.3656 (4)
H_1	0.0706	0.3682	0.1849
H_2	0.0375	0.1651	−0.0666
H_3	0.0585	0.1406	0.2028
H_4	−0.2910	0.2356	0.3944
H_5	−0.1565	0.1876	0.4972
H_6	−0.1823	0.4211	0.2760
H_7	−0.0696	0.3881	0.4858
(b) HOR			
	x/*a*	*y*/*b*	*z*/*c*
S	−0.17148 (7)	0.11733 (5)	0.10759 (11)
O_1	0.0094 (2)	0.3872 (2)	−0.2755 (3)
O_2	−0.1530 (2)	0.4963 (2)	−0.0687 (4)
N	−0.1203 (2)	0.3510 (2)	0.3184 (3)
C_1	−0.0589 (2)	0.4124 (2)	−0.0912 (4)
C_2	−0.0589 (2)	0.3327 (2)	0.1304 (3)
C_3	0.0011 (2)	0.1820 (2)	0.0863 (4)
C_4	−0.1940 (2)	0.2208 (2)	0.3661 (4)
(c) 111 K			
	x/*a*	*y*/*b*	*z*/*c*
S	−0.17212 (7)	0.11696 (6)	0.10868 (12)
O_1	0.0048 (2)	0.3834 (2)	−0.2772 (3)
O_2	−0.1558 (2)	0.4908 (2)	−0.0733 (3)
N	−0.1226 (2)	0.3506 (2)	0.3175 (3)
C_1	−0.0620 (2)	0.4089 (2)	−0.0956 (4)
C_2	−0.0184 (2)	0.3322 (2)	0.1282 (4)
C_3	−0.0020 (3)	0.1818 (2)	0.0881 (5)
C_4	−0.1975 (3)	0.2215 (3)	0.3636 (5)
H_1	0.0648	0.3688	0.1812
H_2	0.0296	0.1613	−0.0829
H_3	0.0534	0.1421	0.2063
H_4	−0.2909	0.2373	0.3826
H_5	−0.1555	0.1834	0.5056
H_6	−0.1843	0.4214	0.2683
H_7	−0.0777	0.3819	0.4866

The average standard deviation of the positional parameters of the hydrogen atoms is 0.025 Å.

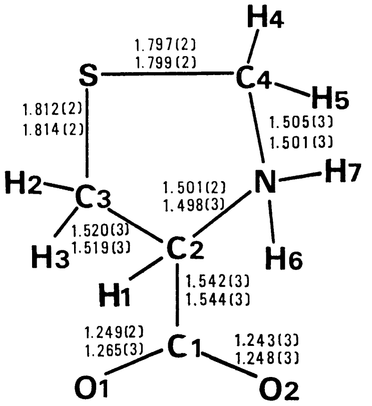

Fig. 1(a). Bond lengths(Å) at 293 K(upper) and 111 K (lower) along with their e.s.d. (in parentheses).

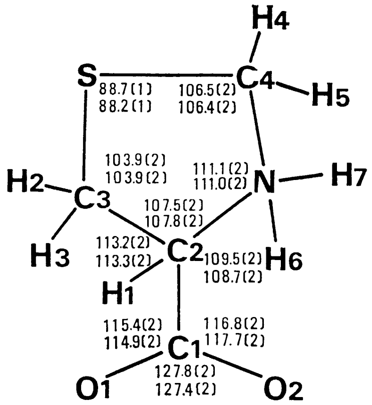

Fig. 1(b). Bond angles(degree) at 293 K(upper) and 111 K(lower) along with their e.s.d. (in parentheses).

Table 5. Equivalent isotropic temperature factors

	293K	111K	HOR
S	1.97	0.802	0.677
O_1	2.17	0.709	0.556
O_2	2.20	0.992	0.817
N	1.19	0.605	0.424
C_1	1.33	0.674	0.428
C_2	1.02	0.502	0.341
C_3	1.68	0.760	0.606
C_4	1.81	0.782	0.603

Each value was estimated from the anisotropic temperature factors.[4]

final parameters of HOR (Figs. 2 and 3). Some density humps probably due to the bonding electrons are found on the C_3–S–C_4 plane. Peaks A and B are situated off the bonds S–C_3 and S–C_4, respectively, in particular deviating from the S–C_4 bond direction. This was found in both the high and low temperature maps, the angles of A–S–B being 105 and 97°, respectively. This indicates that the 3p atomic orbital of the sulfur atom is hybridized with the 3s orbital, the humps due to the bonding electrons deviating from the interatomic vectors as seen in cyclopropane.[5] The difference maps contain some peaks at the center of each atom. This might be caused by the poor accuracy of reflections intensities of high order. This is verified by the difference Fourier synthesis shown in Fig. 4 which was carried out by means of the reflections of $\sin\theta/\lambda < 0.65$. No peaks were observed at the atomic positions. The three maps (Figs. 2, 3, and 4) contain peak D which may be assigned to the lone pair electrons of the sulfur atom.

Population Analysis

The distribution of electron density is defined as a sum of the square of the absolute value of the occupied molecular orbitals.

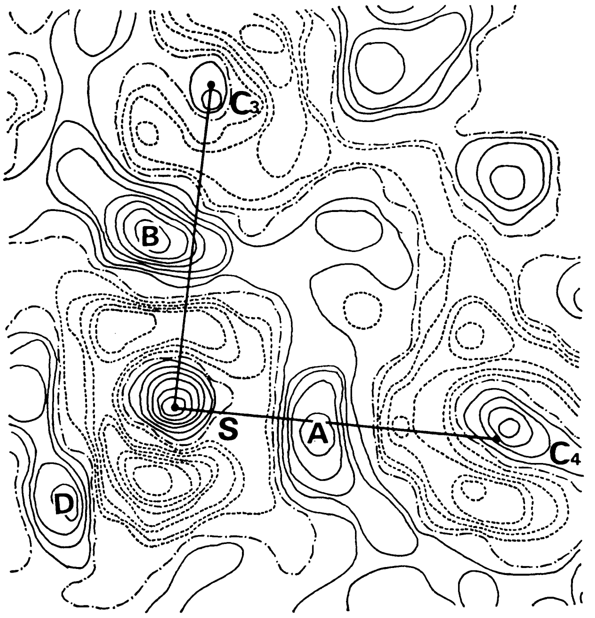

Fig. 2. Difference electron density map in the C_3–S–C_4 plane (111 K). Contours are drawn at the interval of 0.05 $e/\text{Å}^3$. The solid lines are above 0 $e/\text{Å}^3$ and the broken lines are below 0 $e/\text{Å}^3$.

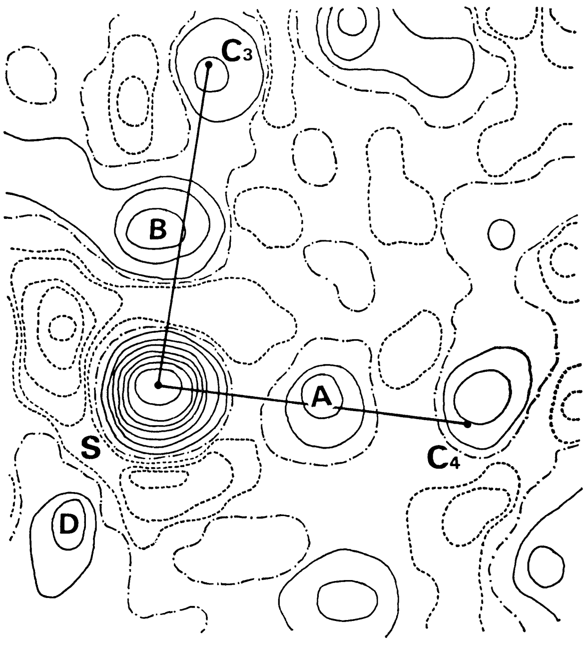

Fig. 3. Difference electron density map in the C_3–S–C_4 plane(293 K).

$$\rho = \sum_{i}^{\text{occupied}} \Psi_i^* \Psi_i \tag{1}$$

The molecular orbital is represented as a liner combination of the atomic basis function ϕ_μ

$$\Psi_i = \sum_{\mu} C_{\mu i} \phi_\mu \tag{2}$$

Substituting Eq. 2 into Eq. 1, we have

$$\begin{aligned} \rho &= \sum_{i}^{\text{occupied}} \sum_{\mu,\nu} C_{\mu i}^* C_{\nu i} \phi_\mu^* \phi_\nu \\ &= \sum_{\mu,\nu} P_{\mu\nu} \phi_\mu^* \phi_\nu \end{aligned} \tag{3}$$

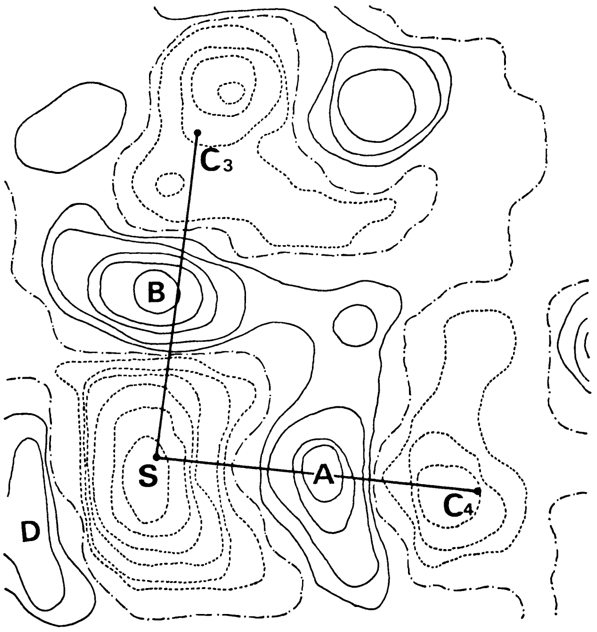

Fig. 4. Difference electron density map in the C_3–S–C_4 plane using only low order reflections($\sin\theta/\lambda<$ 0.65) at 111 K.

$$P_{\mu\nu} = \sum_{i}^{\text{occupied}} C_{\mu i}^* C_{\nu i} \tag{4}$$

where $P_{\mu\nu}$ is a population parameter. The structure factor of the crystal is represented by

$$F_{\text{h}} = \sum_{j,\text{k}} \boldsymbol{F}[\rho_{\text{k}}] \cdot T_{\text{k}j} \cdot \exp(\mathrm{i}s \cdot r_{\text{k}j}) \tag{5}$$

j: atom
k: symmetry operation
$\boldsymbol{F}[\rho_{\text{k}}]$: molecular transform
$T_{\text{k}j}$: temperature factor

where

$$\begin{aligned} \boldsymbol{F}[\rho] &= \sum_{\mu,\nu} P_{\mu\nu} \boldsymbol{F}[\phi_\mu^* \phi_\nu] \\ &= \sum_{\mu,\nu} P_{\mu\nu} \int \phi_\mu^* \phi_\nu \exp(\mathrm{i}s \cdot r) \mathrm{d}r \\ &= \sum_{\mu,\nu} P_{\mu\nu} X_{\mu\nu} \end{aligned} \tag{6}$$

$X_{\mu\nu}$ is called the generalized structure factor. In the population analysis developed by Stewart,1) the structure factor, F_{h}, is separated into two parts, F_{h}(atom) and F_{h}(bond), the former consisting of the atomic orbitals from one atom only, and the latter showing the effect of the overlap between orbitals of the bonded atoms. As a whole, considering the anomalous effects, F_{h} is written as follows.

$$F_{\text{h}} = F_{\text{h}}(\text{atom}) + F_{\text{h}}(\text{bond}) = A + \mathrm{i}B, \tag{7}$$

$$\begin{aligned} A = \sum_{j,\text{k}} [(&f_{\text{core},j} + f_j' + P_{\text{v}j} f_{\text{v}j} - 3 f_{\text{np},\text{np},j} Q_{\text{k}j}) \cdot \\ &\cos(2\pi h r_{\text{k}j}) \cdot T_{\text{k}j} - (f_j'' + \sqrt{3} f_{\text{ns},\text{np},j} D_{\text{k}j}) \cdot \\ &\sin(2\pi h r_{\text{k}j}) \cdot T_{\text{k}j}] + \sum_{m} b_m f_{\text{bond},m} \sum_{\text{k}} \cos(2\pi h r_{\text{k}m}) \cdot T_{\text{k}m}, \end{aligned}$$

$$\begin{aligned} B = \sum_{j,\text{k}} [(&f_{\text{core},j} + f_j' + P_{\text{v}j} f_{\text{v}j} - 3 f_{\text{np},\text{np},j} Q_{\text{k}j}) \cdot \\ &\sin(2\pi h r_{\text{k}j}) \cdot T_{\text{k}j} - (f_j'' + \sqrt{3} f_{\text{ns},\text{np},j} D_{\text{k}j}) \cdot \\ &\cos(2\pi h r_{\text{k}j}) \cdot T_{\text{k}j}] + \sum_{m} b_m f_{\text{bond},m} \sum_{\text{k}} \sin(2\pi h r_{\text{k}m}) \cdot T_{\text{k}m}, \end{aligned}$$

$$f_{\text{core}} = 2X_{1\text{s},1\text{s}} \text{ or } 2X_{1\text{s},1\text{s}} + 2X_{2\text{s},2\text{s}} + 6X_{2\text{p},2\text{p}},$$

$f_v = aX_{ns,ns} + bX_{npx,npx} + cX_{npy,npy} + dX_{npz,npz}$,

a, b, c, d:	the scattering of electrons in each orbital
$f_{ns,np}$:	the scattering effect due to the overlap between ϕ_{ns} and ϕ_{np}
$f_{np,np}$:	the scattering effect due to the overlap between ϕ_{npx} and ϕ_{npy}, or ϕ_{npy} and ϕ_{npz}, or ϕ_{npz} and ϕ_{npx}
f_{bond}:	the scattering factor of the postulated orbital at the center of the bond (r_m)

TABLE 6. POPULATION ANALYSIS REFINEMENT (111K)

	R_w[a]	Scale of $\|F_o\|$
ELS	2.28	0.839
OCR	2.07	0.841
TCR	2.06	0.841
b)	2.76	0.819
HOR	5.26	0.895

a) $R_w = (\sum w \| |F_o| - |F_c| \| / \sum |F_o|) \times 100.0$. b) Value obtained by the usual refinement.

TABLE 7. EXPERIMENTAL AND THEORETICAL POPULATION PARAMETERS

	111 K			293 K		
	ELS	OCR	TCR	ELS	OCR	CNDO
Sp_v	6.908	6.990	7.174	6.233	6.202	6.011
d_x		−0.817	−0.607		1.006	−0.211
d_y		−0.042	0.159		0.486	−0.269
d_z		−0.444	−0.842		−0.703	−0.232
q_1		−0.112	−0.095		0.015	
q_2		−0.287	−0.210		0.015	
q_3		0.008	−0.069		−0.014	−0.159
q_4		0.049	0.016		0.143	0.172
q_5		0.232	0.194		0.122	−0.424
O_1p_v	6.158	6.139	5.935	6.247	6.245	6.492
d_x		−0.023	−0.049		0.159	0.231
d_y		0.114	0.171		0.244	−0.086
d_z		−0.322	−0.415		−0.137	−0.361
q_1		0.083	0.158		0.007	
q_2		0.061	0.084		0.021	
q_3		−0.176	−0.035		−0.029	−0.085
q_4		−0.283	−0.428		0.030	0.249
q_5		−0.181	−0.215		0.078	−0.162
O_2p_v	6.121	6.066	5.967	6.258	6.240	6.519
d_x		0.020	0.070		0.107	−0.324
d_y		0.115	0.136		0.278	0.287
d_z		−0.369	−0.536		−0.154	0.039
q_1		0.086	0.082		0.083	
q_2		0.012	0.105		0.103	
q_3		−0.043	−0.033		0.120	0.193
q_4		−0.207	−0.258		−0.143	−0.005
q_5		−0.108	−0.084		0.071	0.083
Np_v	5.077	5.009	5.092	5.079	5.040	4.978
d_x		−0.274	−0.235		0.047	0.039
d_y		−0.077	−0.043		0.223	−0.019
d_z		−0.241	−0.362		−0.265	−0.055
q_1		−0.010	0.029		0.074	
q_2		0.054	0.124		0.066	
q_3		−0.146	−0.310		0.010	0.002
q_4		−0.084	−0.175		−0.136	−0.088
q_5		0.171	0.132		0.104	0.004
C_1p_v	3.626	3.627	3.343	3.622	3.637	3.615
d_x		0.155	0.220		0.269	−0.026
d_y		−0.236	−0.243		0.377	−0.051
d_z		−0.318	−0.570		−0.479	−0.094
q_1		−0.174	−0.063		−0.060	
q_2		0.328	0.358		0.174	
q_3		−0.827	−0.671		0.343	−0.060
q_4		0.056	−0.095		0.107	−0.066
q_5		0.580	0.514		−0.219	0.041
C_2p_v	3.794	3.783	3.792	3.872	3.839	4.008
d_x		−0.063	0.094		0.311	0.022
d_y		0.556	0.709		0.375	0.073
d_z		−0.362	−0.573		−0.207	−0.196
q_1		−0.015	−0.046		0.052	
q_3		−0.199	−0.170		0.143	
q_3		−0.109	−0.143		0.345	−0.013
q_4		−0.114	−0.113		−0.206	0.227
q_5		−0.304	−0.289		0.032	−0.116
C_3p_v	3.818	3.744	3.624	3.806	3.775	3.956
d_x		−0.121	−0.050		0.239	0.053
d_y		0.143	0.192		0.377	−0.018
d_z		−0.245	−0.436		−0.183	−0.024
q_1		−0.109	−0.052		−0.002	
q_2		−0.047	−0.024		0.084	
q_3		−0.996	−0.006		0.183	−0.051
q_4		−0.295	0.145		−0.019	−0.004
q_5		0.219	0.093		0.060	0.012
C_4p_v	3.501	3.458	3.558	3.596	3.635	3.927
d_x		−0.093	0.005		0.128	−0.056
d_y		0.034	0.124		0.156	−0.115
d_z		−0.170	−0.350		0.033	−0.005
q_1		−0.002	−0.038		0.067	
q_2		0.209	0.131		0.194	
q_3		−0.141	−0.057		0.209	−0.094
q_4		−0.161	−0.034		−0.075	0.007
q_5		0.128	0.092		−0.078	0.004
H_1	1.039	1.046	1.044	1.083	1.105	0.963
H_2	1.038	1.078	1.048	1.047	1.076	0.941
H_3	1.010	0.999	1.006	1.074	1.067	0.990
H_4	1.118	1.152	1.158	1.119	1.133	0.962
H_5	0.959	0.957	0.975	1.054	1.016	0.973
H_6	0.967	0.990	1.026	0.940	0.992	0.805
H_7	0.862	0.962	0.903	0.972	0.998	0.860
S-C_3			−0.664			0.559
S-C_4			−0.279			0.588
C_1-O_1			1.131			0.841
C_1-O_2			0.768			0.771
C_1-C_2			0.781			0.563
C_2-N			−1.057			0.547
C_4-N			1.320			0.562
C_2-C_3			0.615			0.726

D_{kj} and Q_{kj} in Eqs. are expressed in terms of parameters d and q in this table.

$$D_{kj} = d_{xj}S_{xsj} + d_{yj}S_{ysj} + d_{zj}S_{zsj}$$

$$Q_{kj} = q_{1j}(S_{xsj}^2 - S_{ysj}^2) + q_{2j}(S_{zsj}^2 - 1/3) + q_{3j}S_{xsj}S_{ysj} + q_{4j}S_{xsj}S_{zsj} + q_{5j}S_{ysj}S_{zsj}$$

S_{xsj}, S_{ysj}, and S_{zsj} are direction consines of the scattering vector to the principal axes of the p_x, p_y, and p_z orbitals of the j-th atom, respectively.

TABLE 8. EXPERIMENTAL AND THEORETICAL CHARGES

Atom	111 K	293 K	CNDO	EN[a)]
S	−0.990	−0.202	−0.011	0.00
O_1	−0.139	−0.245	−0.492	—
O_2	−0.066	−0.240	−0.519	—
N	−0.009	−0.040	0.022	0.48
C_1	0.373	0.363	0.385	0.40
C_2	0.217	0.161	−0.008	0.02
C_3	0.256	0.225	0.044	−0.14
C_4	0.542	0.365	0.073	−0.03
H_1	−0.046	−0.105	0.037	0.07
H_2	−0.078	−0.076	0.059	0.07
H_3	0.001	−0.067	0.010	0.07
H_4	−0.152	−0.133	0.038	0.07
H_5	0.043	−0.016	0.027	0.07
H_6	0.010	0.008	0.195	0.17
H_7	0.038	0.002	0.141	0.17

a) Calculated from the differences in electronegativity of the neighboring atoms with Mulliken's equation.

The parameter P_v is the number of valence electrons associated with the j-th atom. A dipole distortion of these spherical valence electrons is described by D and a quadrupole distortion by Q. The extended L-shell method(ELS) refines P_v after the usual refinement of the positional and thermal parameters. P, Q, and D are treated as adjustable parameters in the one-center refinement(OCR). The two-center refinement (TCR) includes the b_{mk} term as variables in addition to those of OCR.

In the present calculation, the $f_{core,j}$'s of the carbon and nitrogen atoms are taken from those calculated by use of Clementi's analytical SCF atomic orbitals.[6)] f_{vj}'s of these atoms being taken from these calculated by use of the Slater-type atomic orbitals.[7)] f_v of the hydrogen atom is taken from Stewart-Davidson-Simpson's value,[8)] f_{core} and f_v of the sulfur atom are from the Roothaan-Hartree-Fock wave function by Fukamachi[9)] and $f_{ns,np}$ and $f_{np,np}$ are those of Stewart.[10)] In the case of TCR, f_{bond} is taken as $\overline{X_{ns,ns}(s\cdot r)}$ at the center of each bond where $\overline{X_{ns,ns}(s\cdot r)}$ is a spherically averaged value of the overlapping function between the ns-orbital. The population analysis of the present molecule at 111 and 293 K was carried out after the usual refinement, using ELS, OCR, and TCR, successively. The computer program was written by one of the authors (J.K.). The positional and thermal parameters of OCR and TCR are fixed to the values of ELS. The R factors and scale factors after the refinement are given in Table 6. The R factor decreased from that of the usual refinement, the scale factor of $|F_o|$ becoming close to that of HOR.

The population parameters, thus refined, are compared with the theoretical values calculated by the CNDO method (Table 7). Experimental and theoretical charges are given in Table 8. The experimental values show as a whole the same distribution as the theoretical values except for the hydrogen atoms. However, the charge of the sulfur atom in the low-temperature data deviates considerably from that of CNDO and EN, because of errors in $|F_o|$'s and inaccuracy in the scattering factor of the sulfur atom.

The dipole moment of the molecule can be calculated from the charge distribution in the density map. The absolute values of the dipole moment of the molecule, 11.4 Debye at 111 K and 9.3 Debye at 293 K are roughly in line with the theoretical value (13.2 Debye). However, their directions do not agree with each other.

Discussion

In the present work, we used the higher order reflections refinement to reduce the effect of the spread of the electron cloud. The effect, however, still remains in the parameters, in spite of the considerable depression of the temperature factor (Table 5). The population analysis seems to refine the electronic structure of the molecule; the overall scale factor is improved so as to become close to the value of the HOR, the R factor decreasing significantly from the usual refinement. Some discrepancy in distribution is found between the X-ray and theoretical results. In particular, the sulfur atom at 111 K has a more negative charge than that at 293 K and CNDO. This may be explained as follows:

1) The population analysis treats the small differences between the conventionally calculated structure factors and the observed. The data at 111 K have four times weaker intensities than those at 293 K, depending on the size of the crystal used. Though the smaller crystal gives less systematic errors due to absorption and extinction in the data, the experimental errors in the weaker intensities at 111 K may give rise to some discrepancies.

2) The discrepancy may be due to the neglect of the d-orbital of the sulfur atom and the different character between the L- and M-shell orbitals which are not distinguished in the present analysis.

In spite of these discrepancies we can say that the population analysis throws light on the character of the molecule.

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