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Charge Density Distribution of a Polymethine Cyanine Dye: (5-Dimethylamino-2,4-pentadienylidene)dimethylammonium Perchlorate

BY MASAKO HONDA, CHUJI KATAYAMA AND JIRO TANAKA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku 464, Japan

Abstract

$C_9H_{17}N_2^+ . ClO_4^-$ (orange form), $M_r = 252 \cdot 71$, monoclinic, $P2_1/a$, $a = 13 \cdot 671(3)$, $b = 14 \cdot 899(2)$, $c = 6 \cdot 186(2)$ Å, $\beta = 97 \cdot 27(2)°$, $V = 1249 \cdot 9(5)$ Å^3, $Z = 4$, $D_x = 1 \cdot 343$ g cm^{-3}, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71073$ Å, $\mu = 2 \cdot 606$ cm^{-1}, $F(000) = 536$, $T = 140$ K, $R = 0 \cdot 045$ for 4331 independent data. A slight alternation is found in the bond lengths of the conjugated system of the polymethine cyanine dye [C–C distances $1 \cdot 376(2)$, $1 \cdot 399(2)$, $1 \cdot 378(2)$ and $1 \cdot 394(2)$ Å at 140 K]. The charge distribution is estimated by the method of Coppens, Guru Row, Leung, Stevens, Becker & Yang [*Acta Cryst.* (1979), A35, 63-72] and the result is in good agreement with the *ab initio* MO calculation. In particular, positive charges are found at the methyl groups [except C(11)] and the odd-numbered C atoms in the chain; negative charges are observed at C(4), C(11) and the N atoms.

Introduction

The crystal structure of the title compound (5DMP) is of particular interest because it provides a prototype of the cyanine dye structure. It has several modifications. The structure of the orange form of the perchlorate and that of the chloride were studied by Kulpe and co-workers (Sieber, Kutschabsky & Kulpe, 1974; Ziemer & Kulpe, 1975). The structure of the yellow form of the perchlorate was studied by Selzer & Matthews (1976) and Chentli-Benchikha, Declercq, Germain, Van Meerssche & Michel (1977). The orange form has crystal symmetry $P2_1/a$; accordingly, the accurate structure may be found because the crystal symmetry is not coincident with the molecular symmetry. An alternation of the bond length in the conjugated double bonds is important in the structural chemistry of polymethine cyanine dyes, and a precise X-ray structural study was undertaken on one of the crystal modifications of 5DMP. Recently, Sano & Tanaka (1985) studied the reflection spectra of single crystals of 5DMP, and the orange crystal is found to show an intermolecular charge-transfer band while the yellow form exhibits quasi-metallic reflectivity which is rather unusual for a simple organic dye (Anex & Simpson, 1960). It is important to find the correlation between the crystal structure and spectra for polymorphic crystals.

Coppens and co-workers (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) have proposed a method for estimating the charge distribution in a molecule by an accurate X-ray structure analysis. The cyanine dye has a positive charge in the molecule; therefore, their method may be useful to find the charge distribution in the cation dye. Estimation of the charge distribution in the cation molecule may be a challenge to both the X-ray method and the theoretical study by *ab initio* MO calculation. In this study both methods show excellent agreement, but a few deviations from the predicted charge densities are found which may be ascribed to specific interionic interactions such as hydrogen bonding.

Experimental

The crystals of the orange form grown from a methanol solution were provided by Mr N. Sano. The size of the crystals was less than 0·5 mm and they were polished into a spherical form. The X-ray reflection data were collected by an AFC-5R Rigaku automated four-circle diffractometer at 140 and 296 K. For intensity measurement at 140 K all reflections were measured within a sphere of $2\theta \leq 65°$ and half the sphere was recorded for $65° \leq 2\theta \leq 75°$. A total of 22 525 reflections were measured and averaged to give 6798 independent data. Other experimental conditions are in Table 1. The crystallographic data at 296 and 140 K are shown in Table 2, where we have

Table 1. *Experimental conditions*

	296 K	140(1) K
Data collection		
Crystal size	$0.25 \times 0.30 \times 0.50$ mm	Diameter 0.5 mm
Crystal shape	Prism	Sphere
Diffractometer	Rigaku automated four-circle diffractometer. AFC-5	
Generator	Rigaku rotating-anode X-ray generator, RU-200	
Source	Graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å)	
Scan mode	$2\theta/\omega$ (standard setting)	
Measurement range	$0° \le 2\theta \le 55°$ two independent octants	$0° \le 2\theta \le 65°$ full sphere $65° \le 2\theta \le 75°$ half-sphere
No. of observed reflections	3385	22 525
No. of unique reflections	2985	6798
$R_{\text{int}} = \sum \|F_o\| - \langle \|F_o\| \rangle \| / \sum \|F_o\|$	0.030 for 276 data	0.045 for 5810 data
μ (Mo $K\alpha$)	2.503 cm^{-1}	2.606 cm^{-1}
Range of transmission factors	0.78 ~ 0.89	~0.95
Decay of standard reflections measured after every 100 reflections	Less than 1% (three standard reflections)	Less than 6% (five standard reflections)
Refinement		
Refinement program	Full-matrix least-squares refinement on F^2; SYELS	Full-matrix least-squares refinement on F; RADIEL
Weighting scheme $\sigma^2(\|F_o\|) = \sigma_{cs}^2(\|F_o\|) + (a\|F_o\|)^2$	$w = 1/\sigma^2(\|F_o\|^2)$ $a = 0.020$	$w = 1/\sigma^2(\|F_o\|)$ $a = 0.015$
Refinement variables	206 positional and thermal parameters	235 positional and thermal parameters, valence-electron population (p), valence form factor (κ)
Scattering factors	International Tables for X-ray Crystallography (1974)	Non-H: Fukamachi (1971) H: Stewart et al. (1965)
No. of data used	1986	4331
Criterion	$\|F_o\| \ge 3\sigma(\|F_o\|)$	
R	0.0712	0.0445
wR	0.0697	0.0499
S	2.123	1.301
$(\Delta/\sigma)_{\text{max}}$	0.58 for x of H(11C)	2.5 for U^2 of H(9C)
ρ_{max} (eÅ^{-3})	0.87	0.46

employed the second setting which is different from that of Sieber, Kutschabsky & Kulpe (1974). The structure was refined on F by the full-matrix least-squares program RADIEL (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). The atomic scattering factors of the C and N atoms were divided into core and valence electrons. The population of the valence orbital and the expansion–contraction parameter (κ) were refined. The atomic scattering factors were obtained from the table of Fukamachi (1971) for C, N, O and Cl atoms and from Stewart, Davidson & Simpson (1965) for H. The final atomic parameters, bond lengths and angles are shown in Tables 3 and 4.* All calculations were carried out at the Computation Center of Nagoya University and the Institute for Molecular Science.

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* Lists of H-atom coordinates, non-essential bond lengths and angles, structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42352 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Crystallographic data*

	296 K	140 K
Chemical formula	$C_9H_{17}N_2^+.ClO_4^-$	
Formula weight	252.71	
Z	5	
Space group	$P2_1/a$	
a (Å)	14.039 (1)	13.671 (3)
b (Å)	14.972 (2)	14.899 (2)
c (Å)	6.223 (1)	6.186 (2)
β (°)	96.47 (1)	97.27 (2)
V (Å^3)	1299.7 (3)	1249.9 (5)
D_x (g cm^{-3})	1.292	1.343

Table 3. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
At 296 K				
Cation				
N(6)	0.3723 (2)	0.5008 (2)	−0.6761 (5)	5.3 (1)
N(7)	0.1084 (2)	0.3611 (2)	0.2026 (4)	4.7 (1)
C(1)	0.3130 (3)	0.5079 (3)	−0.5268 (6)	4.7 (1)
C(2)	0.2921 (2)	0.4421 (3)	−0.3851 (5)	4.5 (1)
C(3)	0.2276 (2)	0.4567 (2)	−0.2333 (5)	4.4 (1)
C(4)	0.2029 (2)	0.3937 (2)	−0.0880 (5)	4.5 (1)
C(5)	0.1381 (2)	0.4141 (3)	0.0578 (5)	4.5 (1)
C(8)	0.3884 (4)	0.5773 (4)	−0.8127 (8)	7.7 (2)
C(9)	0.4233 (4)	0.4191 (4)	−0.7117 (8)	7.0 (2)
C(10)	0.0367 (4)	0.3908 (4)	0.3406 (7)	6.5 (1)
C(11)	0.1408 (4)	0.2694 (4)	0.2348 (9)	7.2 (1)
Anion				
Cl(1)	0.11346 (6)	0.69212 (6)	0.20596 (15)	5.29 (3)
O(2)	0.0678 (2)	0.6097 (2)	0.2170 (5)	8.5 (1)
O(3)	0.0494 (3)	0.7596 (3)	0.1852 (9)	14.3 (2)
O(4)	0.1811 (3)	0.7080 (2)	0.3815 (6)	10.6 (1)
O(5)	0.1609 (4)	0.6899 (4)	0.0191 (7)	15.2 (2)
At 140 K				
Cation				
N(6)	0.3739 (1)	0.4958 (1)	−0.6765 (2)	2.7 (3)
N(7)	0.1040 (1)	0.3556 (1)	0.2038 (2)	2.3 (2)
C(1)	0.3133 (1)	0.5030 (1)	−0.5253 (2)	2.2 (2)
C(2)	0.2909 (1)	0.4361 (1)	−0.3864 (2)	2.2 (2)
C(3)	0.2260 (1)	0.4515 (1)	−0.2329 (2)	2.1 (2)
C(4)	0.1995 (1)	0.3878 (1)	−0.0898 (2)	2.2 (2)
C(5)	0.1342 (1)	0.4093 (1)	0.0583 (2)	2.2 (2)
C(8)	0.3917 (1)	0.5720 (1)	−0.8144 (3)	3.6 (4)
C(9)	0.4237 (1)	0.4127 (1)	−0.7178 (3)	3.3 (4)
C(10)	0.0322 (1)	0.3858 (1)	0.3443 (2)	3.0 (3)
C(11)	0.1346 (1)	0.2621 (1)	0.2288 (3)	3.1 (3)
Anion				
Cl(1)	0.11761 (2)	0.68801 (2)	0.20628 (2)	2.41 (5)
O(2)	0.0713 (1)	0.6033 (1)	0.2255 (2)	3.6 (2)
O(3)	0.0464 (1)	0.7568 (1)	0.1925 (3)	6.6 (3)
O(4)	0.1898 (1)	0.7045 (1)	0.3890 (2)	4.1 (3)
O(5)	0.1644 (1)	0.6870 (1)	0.0134 (2)	7.6 (6)

Results and discussion

Crystal structure

The crystal structure projected along the c axis is shown in Fig. 1. The dye cation forms stacked columns along the c axis and the side views of the cation dye and the perchlorate anion are illustrated in Fig. 2. It is remarkable that the ClO$_4^-$ ions are situated at both ends of the cyanine dyes; therefore, the influence of the perchlorate may be larger for the outer dimethylamino groups than for the inner. The

Table 4. *Bond lengths (Å) and angles (°)*

	296 K	140 K
Cation		
C(1)–C(2)	1·375 (5)	1·376 (2)
C(2)–C(3)	1·398 (5)	1·399 (2)
C(3)–C(4)	1·378 (5)	1·378 (2)
C(4)–C(5)	1·389 (5)	1·394 (2)
C(1)–N(6)	1·320 (5)	1·330 (2)
C(5)–N(7)	1·304 (5)	1·310 (2)
N(6)–C(8)	1·459 (6)	1·459 (2)
N(6)–C(9)	1·464 (6)	1·451 (2)
N(7)–C(10)	1·447 (7)	1·462 (2)
N(7)–C(11)	1·452 (6)	1·457 (2)
Anion		
Cl(1)–O(2)	1·396 (3)	1·424 (1)
Cl(1)–O(3)	1·349 (4)	1·409 (1)
Cl(1)–O(4)	1·385 (4)	1·424 (1)
Cl(1)–O(5)	1·404 (5)	1·424 (1)
Cation		
N(6)–C(1)–C(2)	126·2 (4)	126·1 (1)
C(1)–C(2)–C(3)	121·5 (3)	121·0 (1)
C(2)–C(3)–C(4)	124·5 (3)	124·3 (1)
C(4)–C(5)–N(7)	127·0 (3)	126·5 (1)
C(8)–N(6)–C(1)	119·9 (4)	120·9 (1)
C(1)–N(6)–C(9)	122·6 (4)	122·7 (1)
C(9)–N(6)–C(8)	117·6 (4)	116·4 (1)
C(5)–N(7)–C(10)	121·0 (3)	121·0 (1)
C(10)–N(7)–C(11)	115·6 (4)	123·1 (1)
C(11)–N(7)–C(5)	123·5 (4)	115·9 (1)
Anion		
O(2)–Cl(1)–O(3)	111·2 (2)	109·8 (1)
O(2)–Cl(1)–O(4)	113·0 (2)	110·9 (1)
O(2)–Cl(1)–O(5)	106·5 (3)	108·2 (1)
O(3)–Cl(1)–O(4)	109·8 (3)	109·1 (1)
O(3)–Cl(1)–O(5)	108·2 (3)	109·7 (1)
O(4)–Cl(1)–O(5)	108·1 (3)	109·1 (1)

Table 5. *Selected intermolecular distances (Å)*

	296 K	140 K	140 K/296 K
Cation···anion			
C(5)–O(2^i)	3·279 (5)	3·222 (2)	0·983
C(5)–O(2^{ii})	3·208 (5)	3·124 (2)	0·974
C(8)–O(3^{iii})	3·329 (7)	3·310 (2)	0·994
C(8)–O(5^{iv})	3·659 (8)	3·591 (3)	0·981
C(10)–O(2^i)	3·405 (6)	3·380 (2)	0·993
C(10)–O(2^{ii})	3·612 (5)	3·632 (2)	1·006
C(10)–O(2^v)	3·262 (6)	3·172 (2)	0·972
C(10)–O(5^{ii})	3·574 (7)	3·433 (2)	0·961
C(11)–O(3^{ii})	3·546 (7)	3·369 (2)	0·950
C(11)–O(4^{vi})	3·385 (7)	3·265 (2)	0·965
C(11)–O(5^{vii})	3·558 (8)	3·477 (3)	0·977
In column			
C(3)–C(8^{viii})	3·726 (6)	3·683 (2)	0·988
C(4)–C(9^{viii})	3·683 (6)	3·611 (2)	0·980
C(5)–C(1^{viii})	3·640 (5)	3·602 (2)	0·990
C(10)–C(2^{viii})	3·870 (6)	3·789 (2)	0·979
C(10)–C(3^{viii})	3·685 (6)	3·614 (2)	0·981
C(11)–C(2^{viii})	3·958 (6)	3·957 (2)	1·000
Between columns			
N(6)–N(6^{ix})	3·985 (6)	3·843 (2)	0·964
N(6)–C(9^{ix})	3·733 (6)	3·709 (2)	0·994
C(1)–C(9^{ix})	3·983 (6)	3·924 (2)	0·985
C(8)–C(9^{ix})	3·962 (7)	3·893 (2)	0·983
C(8)–C(11^x)	3·886 (8)	3·808 (2)	0·980
C(9)–C(11^{xi})	4·199 (8)	3·930 (3)	0·936

Symmetry operators

(i)	x,	y,	z	(vii)	$0·5-x$,	$-0·5+y$,	$-z$
(ii)	$-x$,	$1-y$,	$-z$	(viii)	x,	y,	$1+z$
(iii)	$0·5+x$,	$1·5-y$,	$-1+z$	(ix)	$1-x$,	$1-y$,	$-1-z$
(iv)	x,	y,	$-1+z$	(x)	$0·5-x$,	$0·5+y$,	$-1-z$
(v)	$-x$,	$1-y$,	$1-z$	(xi)	$0·5+x$,	$0·5-y$,	$-1+z$
(vi)	$0·5-x$,	$-0·5+y$,	$1-z$				

stacking of the dye molecules within the column is significant. The interplanar distances are 3·61(1) (296 K) and 3·56(1) Å (140 K).

On cooling the crystal, the lattice constants vary as shown in Fig. 3. Only the *a* axis shrinks on lowering the temperature and the structure analysis revealed
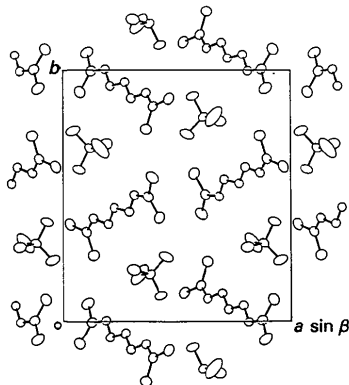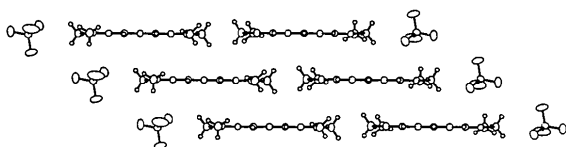
that the distances between the cation and the anion are shortened through electrostatic interaction and/or hydrogen bonding. The changes of interatomic distances are listed in Table 5 and it should be noted that the largest contraction occurs between C(11) of the methyl group and O(4) of the perchlorate anion where the bifurcated hydrogen bonding is expected (Fig. 4).

Molecular structure

The cyanine molecule is completely planar; the best plane includes atoms N(7), C(5), C(4), C(3),

Fig. 1. Projection of the crystal structure along the *c* axis.

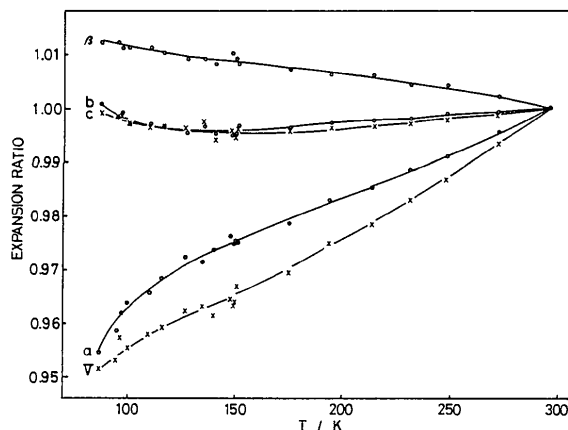Fig. 2. Side view of the arrangement of the dye cations and perchlorate anions.

Fig. 3. Change of lattice constants with temperature. The expansion ratio is defined with respect to the value at 296 K.

C(2), C(1) and N(6) and is given by

$$0.683x + 0.309y + 0.662z - 3.449 = 0 \quad \text{at 296 K}$$

and

$$0.688x + 0.283y + 0.668z - 3.196 = 0 \quad \text{at 140 K,}$$

where the x, y and z axes are taken parallel to the a, b and c^* axes.

The deviations of the skeletal atoms from the plane are less than 0.006 Å. The end C atoms of the methyl groups are on the same plane with deviations of 0.04–0.05 Å. One of the H atoms of the three methyl groups is almost coplanar with the plane as shown in Fig. 5. All methyl groups take a conformation capable of hyperconjugation with the double-bond system; three of them have a pseudo-π orbital composed of the two C–H orbitals while one has a pseudo-π orbital composed of the three C–H bonds (Fig. 5).

The bond lengths shown in Fig. 5 and Table 4 exhibit a slight alternation; the C(5)–N(7) bond length in the polar environment is less than the C(1)–N(6) bond by 0.02 Å, and the C–C bond lengths show a small but clear alternation (0.016–0.023 Å) which is larger than the standard deviation (0.002 Å). For many cyanine dyes, the bond lengths were not discussed because the molecular symmetry coincides with the crystal symmetry or they were not so accurately determined as to be able to discuss the bond alternation (Smith, 1974; Smith & Luss, 1972; Kaneda, Yoon & Tanaka, 1977). The average C–N bond length in the conjugated system is 1.32 Å; that is, equal to the commonly accepted value for a partial double C–N bond of 1.322(3) Å. The C–N single-bond lengths are in the range 1.45–1.46 Å and are slightly shorter than the normal value of 1.472(5) Å (Kennard, Watson, Allen, Isaacs, Motherwell, Petterson & Town, 1972).

Charge density analysis

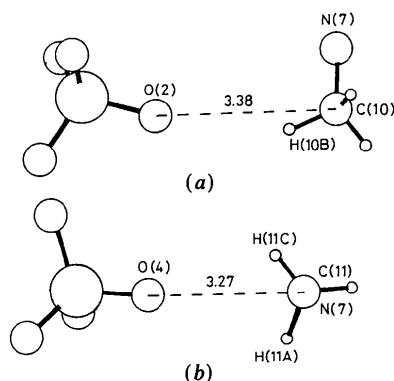Charge distribution in the cation dye was analyzed by the program *RADIEL* (Coppens, Guru Row,

Leung, Stevens, Becker & Yang, 1979) in which population and form factors in each valence orbital of the C and N atoms were refined. The charge on the perchlorate ion was fixed. The final result is shown in Table 6 together with the values calculated by the *ab initio* MO method with STO-3G base (Tanaka, Honda, Katayama, Matsuzaki & Hirao, 1985). In this refinement the populations of the H atoms were fixed as 1.0, while the charge density provided by the Mulliken population analysis shows a significant loss of electrons from the H atoms. It is considered that the experimentally determined charge density on the C atoms includes the total charges associated with the CH or CH_3 groups. The calculated values for the C and H atoms are summed over each group site, and they are compared in Table 6 with the experimental values. The agreement between the experimental charge density with the STO-3G *ab initio* MO result is so excellent that both methods seem to be reliable. It is remarkable that the positive charges are found at the methyl groups [except $C(11)H_3$] and the odd-numbered C atoms in the chain. Negative charges are observed at C(4), the N atoms in the chain and C(11).

The polarization of the charge distribution is of great interest from the point of view of both theoretical and structural chemistry. The MO calculation gives the charge distribution for π and σ electrons as shown in Table 6. It is noticed that the π and σ bonds are oppositely polarized in the conjugated double bond. It is also interesting that the Pariser–Parr–Pople (PPP) method gives fairly correct values for the π-electron distribution. The present experimental technique combined with *ab initio* MO calculations may provide a new method for studying charge polarization in the chemical bond.

Interionic interaction and hydrogen bonding

Close interionic distances between the polymethine dye and the perchlorate ions are shown in Table 4.
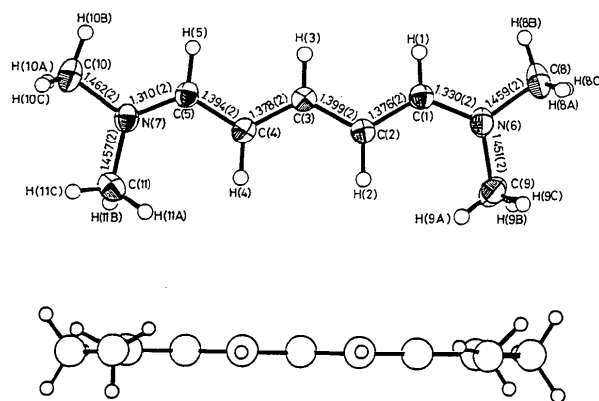

Fig. 4. The CH···O hydrogen bonding between the methyl groups and the O atoms of the perchlorate ion. (a) Projection onto the O(2)–C(10)–H(10B) plane. (b) Projection along the line N(7)–C(11). (Distances in Å.)

Fig. 5. Molecular structure and bond lengths (Å) for the skeletal atoms of the dye.

Table 6. *Charge distributions*

| | X-ray experiment | | Ab initio MO (STO 3G) | | | | PPP method |
| | Total charge | Net charge | Total charge | Net charge | | | π |
				π	σ		
C(1)	5·87 (9)	+0·13 (9)	5·88	+0·12	+0·19	−0·07	+0·25
H(1)	1·0*		0·87				
C+H	6·87 (9)	+0·13 (9)	6·75	+0·25			
C(2)	5·93 (7)	+0·07 (7)	6·14	−0·14	−0·21	+0·07	−0·08
H(2)	1·0*		0·91				
C+H	6·93 (7)	+0·07 (7)	7·05	−0·05			
C(3)	5·72 (8)	+0·28	5·98	+0·02	+0·23	−0·21	+0·24
H(3)	1·0*		0·89				
C+H	6·72 (8)	+0·28	6·87	+0·13			
C(4)	6·00 (7)	0·00 (7)	6·15	−0·15	−0·21	+0·06	−0·08
H(4)	1·0*		0·91				
C+H	7·00 (7)	0·00 (7)	7·06	−0·06			
C(5)	5·85 (8)	+0·15	5·85	+0·15	+0·22	−0·07	+0·28
H(5)	1·0*		0·87				
C+H	6·85 (8)	+0·15	6·72	+0·28			
N(6)	7·17 (7)	−0·17 (7)	7·19	−0·19	+0·38	−0·57	+0·20
N(7)	7·14 (7)	−0·14 (7)	7·19	−0·19	+0·42	−0·61	+0·18
C(8)	5·78 (7)	+0·22 (7)	6·19	−0·19	−0·13	−0·06	
H(8A)	1·0*		0·86				
H(8B)	1·0*		0·87				
H(8C)	1·0*		0·87				
C+3H	8·78 (7)	+0·22 (7)	8·79	+0·21			
C(9)	5·63 (9)	+0·37 (9)	6·32	−0·17	−0·15		
H(9A)	1·0*		0·83				
H(9B)	1·0*		0·83				
H(9C)	1·0*		0·84				
C+3H	8·63 (9)	+0·37 (7)	8·82	+0·28			
C(10)	5·72 (8)	+0·28	6·22	−0·22			
H(10A)	1·0*		0·85				
H(10B)	1·0*		0·86				
H(10C)	1·0*		0·85				
C+3H	8·72 (8)	+0·37 (8)	8·78	+0·22			
C(11)	6·18 (9)	−0·18	6·24	−0·24	−0·14	−0·10	
H(11A)	1·0*		0·85				
H(11B)	1·0*		0·85				
H(11C)	1·0*		0·84				
C+3H	9·18 (9)	−0·18 (9)	8·78	+0·22			

* The electron population of H atoms was fixed at 1·0 in the X-ray analysis.

The distances less than 3·4 Å between the O and C atoms may be regarded as CH···O hydrogen bonding, because they are shorter than the sum of the van der Waals radii of O and the methyl groups. The C(10)···O(2) distance is 3·38 Å at 140 K and O(2)···H(10B) is 2·52 Å, which are reasonable values for CH···O hydrogen bonding. The arrangement of the CH···O atoms is shown in Fig. 4 for two examples, where the distances O(4)···H(11C) and O(4)···H(11A) are 2·80 and 2·95 Å, respectively. The C(11)···O(4) distance [3·385(7) Å at 296 K] shrinks by 3·5% on cooling the crystal. The shrinkage along the a axis on cooling is considered to be due to hydrogen bonding of this type. The net charge distribution on the C(11)H₃ group is negative as shown in Table 6, which is in contradiction with the *ab initio* MO calculation where no intermolecular effect is taken into account. An accumulation of charge at the X–H bond in X–H···Y hydrogen bonding in a weaker or moderately strong hydrogen bond has been noticed in the past several years (Olovsson, 1980; Stevens & Coppens, 1980). These results may be interpreted by the mechanism presented by us (Nukasawa, Tanaka & Nagakura, 1953). In the present analysis a deformation density in the C–H bond region is not so evident due to a lack of sufficient reflection data; however, an accumulation of the charge in the CH₃ region as a whole is consistent with a view of electron migration into the X–H antibonding orbital (Nukasawa, Tanaka & Nagakura, 1953).

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How to Avoid Unnecessarily Low Symmetry in Crystal Structure Determinations

BY WERNER H. BAUR

Department of Geological Sciences, Box 4348, University of Illinois at Chicago, Illinois 60680, USA

AND EKKEHART TILLMANNS*

Institut für Geowissenschaften, Postfach 3980, Universität Mainz, D-6500 Mainz, Federal Republic of Germany

Abstract

A check of recent volumes of *Acta Crystallographica* and *Crystal Structure Communications* shows that about 3% of all recently published crystal structures were described with too low symmetry. Three categories of error are recognized: (1) both Laue class and crystal system are wrong; (2) only the Laue class is wrong; (3) Laue class and crystal system are correct, but an inversion center is missing. Category (1) cases can be most easily diagnosed by calculating the reduced cell and its Niggli matrix. Category (3) cases are most easily recognized during full-matrix least-squares refinement from singularities, high correlations between parameters and poor convergence. The omission of an inversion center will not result in a singular matrix when all atoms in the centrosymmetric cell are in special positions which become general positions in the noncentrosymmetric cell. Once the refinement is completed structures with a missing inversion center can be recognized by unusually high e.s.d.'s, especially for the highly correlated parameters, and by large distortions of observed bond distances and angles from accepted values. Such distortions often show up as splitting of the centrosymmetrically related atomic positions into positions whose average is close to the true centrosymmetric positions. A mechanical application of the *R*-ratio test should be avoided; it can easily lead to wrong conclusions. Proof of higher symmetry must be obtained from the diffraction data. The presence of more than one effective formula per asymmetric unit should always be reason to check for higher symmetry. Cases in all three categories can be checked for the occurrence of higher symmetry by searching for regularities in bond lengths and angles or in the positional coordinates of the atoms. The most systematic way for such searches is the simple, but powerful method of topological analysis of crystal structures. For six structures which previously had been described with too low symmetry higher-symmetry descriptions are provided.

Introduction

In the last several years it was pointed out repeatedly that a number of published crystal structure determinations had been performed with space groups of incorrectly low symmetry. Examples have been given by Marsh and co-workers [Marsh & Schomaker

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* Present address: Mineralogisches Institut, Universität Würzburg, Am Hubland, D-8700 Würzburg, Federal Republic of Germany.