

Difference Densities by Least-Squares Refinement. II. Tetracyanocyclobutane

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The molecular difference density in tetracyanocyclobutane, expanded in a flexible basis of localized deformation functions centred on the atoms, has been derived by least-squares refinement from X-ray data on a crystal cooled to about 165K. The 1781 independent reflexions recorded diffractometrically with Mo $K\alpha$ radiation have permitted the simultaneous determination of the charge distribution and the anisotropic atomic vibrations despite large correlations between the corresponding parameters. An attempt to derive the internal vibrations from an empirical force field was only partly successful. Bond lengths have been corrected for internal vibration, which is particularly significant for the C \equiv N bond. The cyclobutane ring is planar and square. The observed deformation density near the bonds closely matches theoretical maps of the corresponding portions of the molecules cyclobutane, HCN and NCCN. Sharp peaks and shallow valleys around each atomic centre conform to a consistent pattern of angular polarization that builds up a few bond and lone-pair maxima at the expense of a diffuse nearly spherical envelope of charge depletion. Gross charge displacements result in a moderately polar $\bar{C}-\overset{+}{H}$ bond and a strongly polar $\overset{+}{C}\equiv\bar{N}$ group.

Introduction

In part I (Hirshfeld, 1971) a refinement procedure was described that permits the charge-density redistribution accompanying molecule formation to be incorporated in the crystallographic model for least-squares refinement together with the usual positional and thermal parameters. In a trial application to the room-temperature X-ray data from a crystal of fumaramic acid, the method yielded a more detailed map of the deformation density $\delta\rho$ than could be obtained from the same data by standard refinement methods. This map showed features of charge migration in general accord both with theoretical expectations and with experimental results on other structures.

The present study applies the same method to the structure of *cis-trans-cis*-1,2,3,4-tetracyanocyclobutane, which has been determined at room temperature by Greenberg & Post (1968). Several factors make the results of this study more accurate and more complete than those of fumaramic acid. Most important is the low temperature at which the diffraction data were measured, approximately 165K, with the consequent increase in the number and quality of high-angle data recorded. Another advantage is the molecular symmetry, which may be taken as effectively $2/m$ although the site symmetry is only $\bar{1}$. Also, several basic improvements in the charge deformation model have helped to overcome convergence difficulties that marred the earlier study. Far less uncertainty than was anticipated has resulted from the undoubted occurrence of low-frequency internal molecular vibrations, which can be neither neglected nor satisfactorily predicted.

A preliminary account of this study was presented to the First European Crystallographic Conference (Harel & Hirshfeld, 1973).

Experimental

A single crystal of tetracyanocyclobutane, of minimum and maximum dimensions 0.13 and 0.25 mm, was mounted on an Enraf-Nonius CAD-3 three-circle diffractometer linked to an IBM 1800 time-sharing computer. The crystal was cooled by a stream of cold air directed at it from below. The supply Dewar, liquid-level controller, and vacuum-jacketed cold-air line were supplied by Enraf-Nonius and have been described by van Bolhuis (1971). The entire diffractometer was enclosed in a polyethylene tent flushed continuously with dry air at about 10% relative humidity. This arrangement permitted round-the-clock computer-controlled operation for periods of several days with only occasional human intervention. By indirect measurement the temperature of the crystal was estimated to be near 165K.

The space group is $P2_1/n$ and the unit cell contains two centrosymmetric molecules. Cell dimensions were determined from 18 moderately high-angle reflexions ($49^\circ < \theta < 66^\circ$) measured with Cu $K\alpha$ radiation, $\lambda(\alpha_1) = 1.54050$, $\lambda(\alpha_2) = 1.54434$ Å. These gave $a = 8.7267$ (6), $b = 6.1227$ (7), $c = 6.9453$ (6) Å, $\beta = 98.458$ (8)°.

For intensity measurements, graphite-monochromated Mo $K\alpha$ radiation was used, with the reflexion plane of the monochromator perpendicular to that of the specimen crystal. The latter was mounted with $[10\bar{1}]$ along the ϕ axis of the diffractometer. Each reflexion was measured with an $\omega/2\theta$ scan, followed by a background 2θ scan with ω offset 0.6° from the reflecting position. The scan range was 1.4° in 2θ plus the calculated α_1 - α_2 separation and was scanned in steps of 0.02° with 200 ms counting time at each step. The 2θ scan range, step width, and counting time were identical for intensity and background counts at each reflexion.

The measured intensities were corrected for crystal absorption by the Gaussian quadrature method described by Coppens, Leiserowitz, & Rabinovich (1965). This correction was entirely negligible as the transmission factor was found to range between 0.978 and 0.988. No extinction error was recognized and no correction was therefore made, but an error of up to ~3% in the strongest intensities could probably have been absorbed by the refinement parameters and so escaped detection. No account was taken of the beam polarization introduced by the graphite monochromator, thought to be unimportant for Mo radiation.

In the first stage, complete data out to $\theta=35^\circ$ were collected for one hemisphere in reciprocal space, providing at least two equivalent readings (at hkl and $h\bar{k}l$) for each reflexion, except those with $k=0$. After collation of all data from this run, apparent discrepancies were noted and the suspect reflexions, together with all $h0l$ reflexions, were remeasured twice. In most cases the observed discrepancies were judged to fall within acceptable tolerances and all four or more readings of a reflexion were averaged. In a very few instances one of the discordant readings was clearly spurious and was discarded.

After preliminary refinement of the structure (standard positional and thermal parameters only) against the 1616 independent reflexions at $\theta < 35^\circ$ measured in the first two runs, structure factors were computed out to $\theta=50^\circ$. Of nearly 2000 reflexions between 35 and 50° , 165 had values of $|F_c|$ exceeding 3.0. These were then measured in the same way as the earlier data, except that the counting time was doubled in this final run to 400 ms per step for greater statistical precision.

From an extensive comparison of the individual readings for the same or symmetry-equivalent reflexions the random error in a single observation was estimated to comprise a 2% standard deviation in the net intensity in addition to the statistical counting error, *i.e.*

$$\sigma^2(I-B) \sim [0.02(I-B)]^2 + I + B.$$

The statistical weight of each reflexion was taken as the sum of the calculated weights $w=1/\sigma^2$, estimated by the formula above, slightly modified to reflect the degree of concordance of the several observations. Of the 1781 independent reflexions recorded, 108 had,

after averaging, negative values of F_o^2 and 120 more had $F_o^2 < \sigma(F_o^2)$. All were included normally in the least-squares refinements without discrimination (Hirshfeld & Rabinovich, 1973).

Refinement

The refinement began with the coordinates published by Greenberg & Post (1968) and was based throughout on the minimization of

$$\Delta = \sum w(F_o^2 - k^2 F_c^2)^2.$$

In the first stage, standard free-atom f curves were used, except that the hydrogen atoms were contracted as by an effective nuclear charge $\zeta_H = 1.2$. Anisotropic vibration tensors were assigned to all atoms but these were constrained by the assumption of molecular rigidity, so that only 12 molecular vibration components T^{ij} and L_{ij} were adjusted, along with the scale factor k and the 24 atomic coordinates. This rigid-body refinement converged to discrepancy indices:

$$\begin{aligned} R &= \sum |F_o - k|F_c| / \sum F_o = 0.072 \text{ (excluding negative } F_o^2), \\ r &= [\Delta / \sum w F_o^4]^{1/2} = 0.103, \\ d &= [\Delta / (n-p)]^{1/2} = 2.38 \end{aligned}$$

with $n = 1781$, $p = 37$ (Table 1, row *A*).

For comparison, an unconstrained refinement was performed with six independent thermal parameters U^{ij} for each of the eight atoms. This gave the significantly lower discrepancy indices listed in row *B* of Table 1. Comparison of these two results provided the first indication that the rigid-body constraint was inappropriate. However, the fact that both refinements had been performed with spherical atoms left the issue in some doubt.

In the next stage, the spherical-atom charge distribution was modified by the introduction of 36 charge-deformation coefficients as additional least-squares parameters. The basis functions chosen for expanding the deformation density $\delta\rho$ had a Gaussian radial dependence $r^m \exp(-\gamma r^2)$, which has the merit of being more compact and yet less sharply peaked at the atomic centres than the exponential functions used in part I. Combining these with the same angular functions previously used led to 22 expansion functions on each

Table 1. *Discrepancy indices for several refinement models*

For each model, the number p of adjustable parameters is itemized in parentheses in the sequence: scale factor k , coordinates, vibration parameters, and deformation parameters.

Model	Thermal vibrations	Charge deformation	Parameters	$10^4 R$	$10^4 r$	d
<i>A</i>	Rigid molecule	None, $\zeta_H = 1.2$	36 (1 + 24 + 12 + 0)	717	1032	2.380
<i>B</i>	Independent U^{ij}	None, $\zeta_H = 1.2$	73 (1 + 24 + 48 + 0)	628	867	2.019
<i>C</i>	Rigid molecule	Variable net charge	72 (0 + 24 + 12 + 36)	522	620	1.443
<i>D</i>	Rigid molecule	Zero net charge	72 (1 + 24 + 12 + 35)	522	619	1.443
<i>E</i>	Independent U^{ij}	Zero net charge	108 (1 + 24 + 48 + 35)	450	527	1.242
<i>F</i>	Force field + T, L	Zero net charge	72 (1 + 24 + 12 + 35)	507	602	1.402
<i>G</i>	Independent U^{ij}	Zero net charge, modified γ	111 (1 + 24 + 48 + 38)	451	527	1.242
<i>H</i>	Independent U^{ij}	Zero net charge, modified γ and ζ_H	112 (1 + 24 + 48 + 39)	449	525	1.237

atomic centre having, before orthogonalization, the general form

$$g_{m,n}(r, \theta_k) = N_{m,n} r^m \exp(-\gamma r^2) \cos^n(\theta_k)$$

with $m=0, 1, 2$ or 3 ; $n \leq m$; $k=1, 2 \dots (n+1)(n+2)/2$. The functions with n even (corresponding to r_m and v_k of part I) are even and their normalization factors $N_{m,0}$ and $N_{m,2}$ were chosen to make the integral of $g_{m,n}$ over all space equal to one electron. The odd functions $g_{m,1}$ and $g_{m,3}$ (corresponding to λ_k and μ_k) were normalized to have a net charge of half an electron in the halfspace where $\cos \theta_k$ is positive.

In defining the deformation model, the molecule was supposed to comprise four identical HCCN fragments in accordance with its apparent $2/m$ symmetry. Further, each such unit was taken to be symmetric with respect to a local mirror plane, lying essentially perpendicular to the cyclobutane ring. These constraints were not applied to the atomic coordinates, which showed small departures from the symmetric geometry, but only to the deformation density $\delta\rho$ around each atom. Finally, the deformations at the cyano carbon and nitrogen atoms and at the hydrogen atoms were assumed axially symmetric about the respective bond directions. These approximations reduced the number of independent deformation coefficients to 15 for the ring carbon atom, 8 each for the exocyclic carbon and nitrogen atoms, and 5 for hydrogen, on which functions with $m=3$ were omitted (see part I). The underformed reference hydrogen atom was initially given its free-atom exponent $\zeta=1.0$.

The exponential factors γ were not systematically optimized but a fairly extensive series of exploratory refinements produced a set of values giving near minimal discrepancy indices. Trial calculations also showed that the interesting features of the final $\delta\rho$ map were not excessively sensitive to small changes in γ . All but the last two series of calculations reported below used $\gamma=4.0 \text{ \AA}^{-2}$ for hydrogen and carbon, 5.0 \AA^{-2} for nitrogen. These values place the maximum of the most diffuse radial function on each atom (*i.e.* with $m=2$ for hydrogen, $m=3$ for carbon and nitrogen) at a distance $r=(m/2\gamma)^{1/2}$ slightly under half an average bond length from the atomic centre.

Wary of possible convergence difficulties due to severe parameter correlations, we initially reimposed the rigid-body constraint on the vibration parameters and also held the scale factor k fixed at the value obtained from model *A*. Three refinement cycles on the 72 independent parameters yielded the discrepancy indices listed in Table 1, line *C*. Comparison with the results from the two previous models lent strong support to the deformation model, which clearly did far more to improve the agreement between F_o and F_c than assignment of independent U^{ij} to the several atoms.

Attention was next directed at an irksome flaw in the original refinement program: the unphysical variability of the net molecular charge implied by the deformation coefficients. This formal defect was thought largely to

blame for the difficulties encountered in early attempts (part I) to refine the scale factor simultaneously with the deformation coefficients. It also led to small but disconcerting variations in the calculated value of F_{000} even when the scale factor was arbitrarily fixed. (The parameters of model *C* correspond to a net molecular charge of $+0.30 e$, yielding a value of F_{000} , for the two-molecule unit cell, smaller by 0.6 than it should be.) The remedy adopted was suggested by Waser's (1963) use of subsidiary conditions: slack constraints in the terminology of Pawley (1971). It consisted in treating F_{000} as an observed quantity with the appropriate unscaled magnitude and with large statistical weight. This simple device constrained to zero the sum of the coefficients of the even deformation functions, thus reducing from 36 to 35 the effective number of deformation parameters. (The odd functions have vanishing net charge and are unaffected.) As a result the crystal was kept electrically neutral with no other loss in the flexibility of the deformation model. It became possible, as hoped, to relax the constraint on the scale factor and still obtain a stable and entirely reasonable solution. In fact, the modified routine produced a modest 1% drop in k , compared with model *A*, with an estimated standard deviation of 0.3%. The only other appreciable change was a small rise in the estimated standard deviations of the even deformation coefficients, which had been somewhat underestimated in model *C* through the artificial constraint on k . Final discrepancies from this refinement are listed in Table 1, row *D*.

The problem of a proper description of the atomic vibrations still had to be faced. Although other factors, such as systematic errors in the data and incomplete representation of the charge deformation, might also contribute appreciably, the neglected internal vibrations seemed the most likely explanation for the high value of the figure of merit $d=1.44$. This quantity should be nearer to unity if the data were valid (*i.e.* errors randomly distributed and properly reflected in the weights w_{hkl}) and the model appropriate.

The most direct way to test the importance of internal vibrations was simply to remove the rigid-body constraint and continue the refinement with independent atomic vibration components U^{ij} . When this was done the refinement converged smoothly, despite large correlation coefficients between the vibration parameters and the deformation coefficients, to the final discrepancy indices listed in Table 1, line *E*.

Comparison of lines *D* and *E* of Table 1 yields an r factor ratio of $0.062/0.053=1.17$, which, in view of the large number of reflexions, appears to rule out the rigid-body hypothesis at any meaningful level of significance (Hamilton, 1965). We can also test more directly how well the constrained values U^{ij} from model *D* agree with those derived from the unconstrained refinement *E*. If the rigid-body hypothesis were justified these two sets of values should agree to within the accuracy of the latter results. In fact, the ratio of the discrepancies

ΔU^{ij} to the estimated standard deviations $\sigma(U^{ij})$ from refinement E had a r.m.s. value of 3.3 and a maximum of 11.4. Our conclusion must be that internal vibrations contribute significantly to the experimental atomic motion.

There are also independent grounds for doubting the rigidity of the molecule. Crystallographic symmetry requires the cyclobutane ring to be strictly planar even though gaseous cyclobutane itself is known to be bent and to undergo low-frequency puckering vibrations (Lord & Nakagawa, 1963; Ueda & Shimanouchi, 1968). We must suspect that tetracyanocyclobutane may also have a non-planar equilibrium geometry and, in any event, is unlikely to offer strong resistance to out-of-plane deformation of the ring. Bending vibrations of the C-C \equiv N legs are probably also too low in frequency to be negligible.

Consistent force field

While we apparently have no choice but to abandon the rigid-body model, it would be useful to have an alternative model that avoided the opposite extreme of completely independent atomic vibration tensors. The most promising approach appeared to be an attempt to estimate the internal molecular vibrations by use of the consistent force field developed by Lifson & Warshel (1968). This method is based on an empirical molecular force field whose form is deduced from structural, spectroscopic and thermodynamic properties of families of related molecules and from which the equilibrium geometry and dynamic behaviour of other molecules of similar constitution can be predicted. Our attempt to apply this approach to tetracyanocyclobutane had three major objectives.

1. It could, if successful, lead to a detailed account of the vibrational behaviour of the molecule, which would nicely supplement the structural information provided by our crystallographic study.

2. A realistic description of the internal molecular vibrations would form a valid basis for deriving vibrational corrections to the observed molecular dimensions.

3. Knowledge of the atomic vibrations, obtained independently of the X-ray data, could be incorporated in an improved model for least-squares refinement. This would avoid both the systematic shortcomings of the rigid-body model and the large parameter interactions of the completely unconstrained refinement and so lead to more precise values for the remaining least-squares parameters.

Unfortunately, application of the consistent force field to the present problem has encountered formidable obstacles. First, the force field relating to distortions of the cyclobutane ring was not known from previous studies by this method, which had not treated rings of under five atoms. Similarly, the cyano stretching and bending parameters had to be deduced from experimental evidence that was not as extensive or as

dependable as that pertaining to some of the better characterized molecular components. In addition, all signs pointed to the occurrence of some very low-frequency internal vibrations, notably the ring-bending motions, which could not be separated from the lattice modes. Accordingly, any proper treatment of the vibrational behaviour of the molecule in the solid (Warshel & Lifson, 1970) must deal with the intramolecular and intermolecular forces simultaneously. Finally, with much of the atomic motion attributable to these low-frequency modes, calculations restricted to vibrations of zero wave vector are incapable of accounting properly for the expected frequency dispersion across the Brillouin zone. For all these reasons, a definitive description of the dynamics of crystalline tetracyanocyclobutane has not yet been achieved. Thus the first of the three goals set out above still eludes us. Still, enough progress has been made towards the other two objectives to permit the present crystallographic study to proceed to a satisfactory conclusion.

To enable the force field to handle the vibrations of the cyclobutane ring, the stretching, bending, and torsion force constants of the endocyclic C-C bonds were adjusted to fit the known behaviour of cyclobutane itself. The force field so obtained predicted, for gas-phase cyclobutane, an equilibrium dihedral angle of 29°, a harmonic bending frequency of 227 cm⁻¹, and a barrier to planarity of 1.46 kcal mole⁻¹, all in good agreement with spectroscopic results (Ueda & Shimanouchi, 1968; Stone & Mills, 1970; Miller & Capwell, 1971). To this force field were added cyano stretching and bending force constants transferred from the infrared studies of methyl cyanide (Nakagawa & Shimanouchi, 1962) and malononitrile (Fujiyama & Shimanouchi, 1964). Rather larger C-C \equiv N bending force constants have been found by Cyvin & Cyvin (1973) in their study of 2,2-dicyanopropane.

The resulting force field for tetracyanocyclobutane was first required to predict the observed crystal structure. For this test the cell dimensions were fixed at their experimental values and the two molecules in the unit cell were allowed to adjust their shapes and positions, with no space-group constraint, to minimize the total calculated energy (Warshel & Lifson, 1970). The structure so obtained displayed the correct $P2_1/n$ symmetry, with planar cyclobutane rings, the r.m.s. displacement from the observed atomic positions was 0.16 Å, and the three inertial axes of the molecule deviated by 0.9, 5.4 and 5.3° from their true directions.

Satisfied that the force field appeared to represent adequately both intra- and intermolecular potential-energy terms, we next tried several approaches to the dynamical problem of the vibrational behaviour of the molecules in the crystal. None of these approaches attempted a complete description of the lattice dynamics, and all entailed some artificial separation of the translational lattice modes from the internal and librational vibrations. Yet several of these crude attempts at least stood up to our primary crystallographic test:

when inserted in the least-squares program, the calculated vibration parameters allowed the refinement to attain lower discrepancy indices than had been obtained with the rigid-body model, with no increase in the number of adjustable parameters. The procedure adopted in these refinements was to assign to each atom a set of anisotropic vibration components U^{ij} made up of two contributions: a fixed part taken directly from the force-field calculations and a variable part derived from the molecular translation and libration tensors. The latter tensors were included to correct approximately for the known deficiencies in the dynamical treatment of the lattice vibrations and, without being assigned any precise physical meaning, were refined just as in the rigid-body model. The best of these refinements converged to the discrepancy indices listed in Table 1, line *F*.

This result can be judged in exactly the same way as was the rigid-body refinement, by numerical comparison with the unconstrained refinement *E*. Such comparison yields an *r* factor ratio of $0.060/0.053 = 1.14$, while the ratio $|\Delta U^{ij}|/\sigma(U^{ij})$ showed a r.m.s. value of 2.8, a maximum of 8.4. The implication is that this model, while a clear improvement over the rigid-body model, should also be rejected as incompatible with the X-ray evidence.

Nevertheless, it would be misleading to conclude that the consistent force field has yielded a false description of the atomic vibrations. Firstly, our statistical tests rest on the assumption that all errors are randomly distributed. That the lowest value attained by the figure of merit is still $d = 1.24$ (Table 1, line *E*) hints at further systematic error, in the data or in the model. And where systematic error is present, the vibration parameters are notoriously its easiest victims (but see below). Secondly, the actual discrepancies between the values of U^{ij} from refinements *E* and *F* are, even if statistically significant, mainly quite small. Thus the dynamical treatment, for all the crudity of our approximations, has led to atomic vibration tensors in substantial agreement with the unconstrained refinement. This is seen in Table 2, which compares values of U^{ij} from refinements *F* and *H* (see below; the substitution of model *H* for model *E* scarcely affects this comparison as these two models differ inappreciably except for the hydrogen atoms, to which model *E* assigns somewhat smaller average amplitudes, and larger standard deviations, than model *H*). Accordingly, while statistical arguments lead to a slight preference for the unconstrained refinement, the differences between this and the force-field results are small enough that the choice between them is of minor consequence.



Final refinement

To complete the unconstrained refinement it seemed advisable to check again the influence of small changes in the exponential factors γ . A new search in the

Table 2. Atomic vibration components from the force-field calculation (model *F*) and from the final unconstrained refinement (model *H*)

For each atom, U^{ij} in $\text{\AA} \times 10^{-4}$ ($\text{\AA} \times 10^{-3}$ for hydrogen) from models *F* and *H* are listed on successive lines; the latter has estimated standard deviations in parentheses.

	U^{12}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
C(1)	119	143	115	2	10	20
	120 (3)	134 (3)	127 (4)	6 (2)	1 (2)	26 (2)
C(2)	157	133	233	-8	28	73
	157 (3)	133 (4)	219 (4)	2 (2)	33 (2)	80 (2)
C(3)	114	118	144	5	-4	29
	101 (3)	122 (3)	153 (3)	8 (2)	-10 (2)	21 (2)
C(4)	109	221	214	26	55	11
	105 (3)	215 (4)	219 (4)	16 (2)	59 (3)	4 (2)
N(1)	217	152	398	-45	-7	146
	223 (7)	154 (7)	387 (8)	-43 (3)	11 (2)	156 (3)
N(2)	118	465	344	21	126	-30
	123 (7)	465 (9)	311 (8)	-3 (3)	121 (3)	-44 (3)
H(1)	30	40	16	-2	0	0
	35 (7)	34 (8)	18 (8)	0 (5)	-8 (5)	0 (5)
H(2)	30	22	35	0	-10	8
	32 (8)	23 (7)	37 (8)	-4 (5)	-15 (7)	6 (4)

neighbourhood of the values previously used showed that a very slight drop in *r* could be achieved if γ was lowered by 0.5\AA^{-2} for hydrogen and raised a similar amount for nitrogen. The final values adopted were thus 3.5, 4.0 and 5.5\AA^{-2} , respectively, for hydrogen, carbon and nitrogen. The resulting discrepancies (Table 1, line *G*; the indicated number of deformation parameters includes the three γ quantities) were imperceptibly lower than for model *E*. In most other respects, too, such as bond lengths and final $\delta\rho$ map, the change was quite negligible.

The output of this refinement, however, revealed an apparent anomaly in the vibration parameters of the hydrogen atoms. In the course of calculations aimed at estimating bond-length corrections according to the riding model of Busing & Levy (1964), it was necessary to evaluate, for each pair of bonded atoms A and B, the mean square displacements z_A^2 and z_B^2 along the interatomic vector. On any realistic model of the vibrational behaviour, we expect a pair of covalently bonded atoms to undergo very little relative motion along the bond axis. This implies that z_A^2 and z_B^2 should be nearly equal. (The converse does not follow, of course.) This expectation was found to be fulfilled exceedingly well for all C-C and C≡N bonds in the molecule. By contrast, the C-H bonds had discordantly small values of z_H^2 , equal to 0.0073 and 0.0052\AA^2 for H(1) and H(2), respectively, as against values of z_C^2 equal to 0.0134 and 0.0125\AA^2 for C(1) and C(3). This was the more anomalous as z_H^2 is expected to exceed z_C^2 by about 0.005\AA^2 , mainly through the zero-point C-H stretching motion, according to the spectroscopic results presented by Johnson (1970) for cyclobutane. The apparent explanation was that our charge deformation model had inadequately described the very pronounced contraction of the hydrogen charge cloud (Ruedenberg, 1962; Hirshfeld & Rztokiewicz, 1974), which had therefore

expressed itself partly in a systematic underestimate of the hydrogen vibration amplitudes.

Concluding that the Gaussian deformation functions were incapable of representing the enhanced cusp density at the hydrogen nucleus, we augmented the deformation model by again assigning to the hydrogen f curve an effective nuclear charge ζ_H greater than 1.0. Parallel refinements, similar to model G , were performed with alternative values of ζ and the lowest discrepancy indices (Table 1, row H) were obtained for $\zeta = 1.30$. The vibration parameters from this model led to values of z_H^2 for the two C-H bonds slightly larger, as expected, than the corresponding values of z_C^2 (Table 3). For all other bonds the agreement between z_A^2 and z_B^2 is even better than would be expected from the estimated standard deviations of U^{ij} (Table 2). This remarkable agreement strongly supports the physical reality of the refined vibration parameters. The implication is that with high-angle X-ray data of sufficient quantity and quality, the simultaneous determination of charge deformations and vibration amplitudes is far less troublesome than had been feared.

Table 3. Mean-square atomic displacements u^2 from model H , resolved into components parallel (z^2) and perpendicular (w^2) to each bond axis $A-B$ for riding-motion analysis

Data for ring bonds C(1)-C(3) and C(1)-C(3') included for comparison of z_A^2 and z_B^2 only. All quantities in $\text{Å}^2 \times 10^{-4}$.

A-B	u_A^2	u_B^2	z_A^2	z_B^2	w_A^2	w_B^2	Δw^2
C(1)-C(3)	379	375	130	134	249	241	
C(1)-C(3')	379	375	113	116	265	259	
C(1)-C(2)	379	493	132	135	246	358	112
C(3)-C(4)	375	545	112	115	264	430	166
C(2)-N(1)	493	732	140	136	353	595	242
C(4)-N(2)	545	922	118	114	427	808	381
C(1)-H(1)	379	878	131	153	247	725	478
C(3)-H(2)	375	919	123	132	253	787	535

We take the new results, designated model H , to represent the final outcome of our X-ray study.*

Molecular dimensions

The uncorrected bond lengths and angles, with their estimated standard deviations, follow directly from the atomic coordinates (Table 4) and the covariance matrix of refinement H . For the vibrational corrections, however, we require detailed knowledge of the internal vibrations and this must come from our force-field calculations. According to Busing & Levy (1964) the corrected average distance s between two vibrating

Table 4. Fractional atomic coordinates from model H (standard deviations in parentheses)

See Fig. 1 for atomic numbering.

	x	y	z
C(1)	0.03514 (8)	0.08568 (12)	-0.12702 (13)
C(2)	0.14877 (10)	0.26016 (15)	-0.12434 (9)
C(3)	0.09262 (9)	-0.12259 (14)	-0.00602 (10)
C(4)	0.25030 (12)	-0.11419 (11)	0.09543 (11)
N(1)	0.24320 (12)	0.39275 (17)	-0.11591 (9)
N(2)	0.37461 (15)	-0.10271 (12)	0.17697 (13)
H(1)	-0.0068 (14)	0.0472 (17)	-0.2643 (32)
H(2)	0.0787 (11)	-0.2601 (32)	-0.0875 (21)

atoms is related to their apparent separation s_0 by the expression

$$s = s_0 + w^2/2s_0.$$

The quantity denoted by w^2 , assumed small, is the mean-square relative displacement of the two atoms projected onto a plane perpendicular to the mean interatomic vector. In principle, we can obtain this quantity by summation over the normal vibration modes, which are assumed independent in phase. But we recall that our dynamical calculation could not deal properly with the lattice vibrations and had to be supplemented by the inclusion of molecular translation and libration tensors whose components were deduced from the X-ray data. Accordingly, the vibrational corrections to the bond lengths (Table 5) had to be derived in two parts, which were applied additively. The first part, Δs_{int} , corrected for the vibration modes explicitly treated in the dynamical calculation; the second, Δs_{lib} , allowed for the extra librational motion implied by the libration tensor from refinement F . The total vibration corrections range from 0.006 to 0.020 Å. Because of the approximations used in the dynamical calculations, the uncertainty in these corrections is rather large, probably greater than the standard deviations of the uncorrected dimensions. We assume a 50% error in the vibration corrections in estimating the standard deviations of the corrected bond lengths, shown in Table 5 and Fig. 1.

We cannot test our estimates of the standard deviations by comparing chemically equivalent bond lengths. Not only are the vibration corrections strongly correlated, because of the symmetry of the intramolecular potential-energy terms, but even the uncorrected bond lengths suffer a measure of statistical interaction due to non-negligible correlations between the atomic coordinates and the deformation coefficients. Thus the pleasing agreement between equivalent bond lengths is no guarantee of the accuracy of our results.

Comparison of the experimental bond lengths (Table 5) with those obtained by Greenberg & Post (1968) (G & P) shows that our uncorrected values are invariably greater than those of G & P and in most cases are close to their *corrected* values. The difference in uncorrected values is in the direction to be expected from the difference in temperature of the two experi-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30614 (31 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ments. But this difference should disappear in the corrected values if both sets of vibration corrections have been properly estimated. G & P based their correction on the riding model of Busing & Levy (1964) and concluded that the correctness of this model 'can only be unambiguously established on the basis of low-temperature work'. The present comparison suggests that this model may have slightly but systematically underestimated the bond-length corrections. But two reservations must be attached to this conclusion. First, we cannot convincingly rule out the alternative explanation that our force-field treatment has severely overestimated the corrections. Second, the corrected bond lengths from the two studies differ, at most, by about twice the present estimated standard deviations.

G & P made no corrections to the lengths of the C-C bonds in the cyclobutane ring. They reported a significant difference of 0.014 Å between the two non-equivalent pairs of bonds, which our study does not confirm. The present difference is only 0.003 Å, entirely without significance. Thus we find the cyclobutane ring to be exactly square, with equal bond lengths and 90° angles (Fig. 1). The average corrected bond length of 1.572 (3) Å agrees with the best values for similar molecules listed by G & P in their Table 1.

The calculated vibration correction is most significant for the two C≡N bonds, where it equals 0.011 and 0.014 Å. This apparent bond shortening arises largely from low-frequency C-C≡N bending vibrations. The customary neglect of such internal vibrations probably accounts for the shortness of most crystallographically determined C≡N bond lengths. The most precise of these determinations typically lie around 1.150 Å or shorter (Filippakis, Leiserowitz & Schmidt, 1967; Hoekstra, Spoelder & Vos, 1972), significantly below the accepted spectroscopic value (Britton, 1967) of 1.158 Å. Our corrected value is 1.162 (6) Å, which appears to err slightly in the opposite direction. Since the aim of the vibration correction, as defined by Busing & Levy (1964), is the average interatomic separation, our result should probably be taken as a measure of r_g . It is not unreasonable that this may be a bit longer than the spectroscopic quantities r_o or r_s (Lide, 1964) but the observed difference is clearly too small to be significant.

The uncertainty of our force-field calculations, coupled with the fact that for many structures even such an approximate dynamical treatment may not be feasible, raises the question of alternative methods for deriving the needed vibrational corrections to the observed bond lengths. In the present structure, if we had the results of model *H* alone we should probably attempt to correct all but the endocyclic bond lengths by means of the riding model of Busing & Levy (1964), just as Greenberg & Post (1968) did for their room-temperature results. We should thus obtain, by way of the calculations detailed in Table 3, the corrections listed in the last two columns of Table 5. These results are rather similar to those from our force-field treatment. The average exocyclic C-C bond length is 1.4570, compared to 1.4595 from the CFF treatment, while the average for the C≡N bonds is 1.1633, as against 1.1622 Å. This comparison indicates that in the absence of a full dynamical treatment, the riding model may often provide a reasonable approximation. This is probably generally true for the C≡N bond and certainly offers a better alternative than the total neglect of the appreciable internal vibrations of the cyano group. Previous applications of the riding model to C≡N bonds have corrected the observed bond lengths

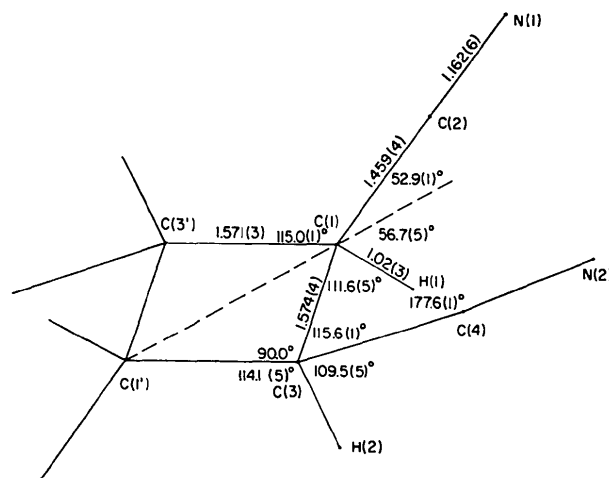


Fig. 1. Bond lengths (corrected) (Å), and angles (°), averaged in accordance with $2/m$ molecular symmetry.

Table 5. Final corrected bond lengths, in Å (standard deviations in parentheses), compared with values from Greenberg & Post (1968)

s_o is the uncorrected value, s includes correction Δs_{int} for internal vibrations plus Δs_{lib} for libration. Last two columns show alternative correction based on the riding model of Busing & Levy (1964).

Bond	G & P (1968)		Present study					
	s_o	s_{rid}	s_o	Δs_{int}	Δs_{lib}	s	Δs_{rid}	s_{rid}
C(1)-C(3)	1.561		1.5662 (12)	0.0051	0.0026	1.5739 (41)		
C(1)-C(3')	1.547		1.5644 (12)	0.0052	0.0012	1.5708 (34)		
C(1)-C(2)	1.448	1.453	1.4540 (13)	0.0050	0.0018	1.4608 (37)	0.0038	1.4578
C(3)-C(4)	1.441	1.451	1.4504 (13)	0.0053	0.0025	1.4582 (41)	0.0057	1.4561
C(2)-N(1)	1.129	1.155	1.1508 (16)	0.0094	0.0015	1.1616 (57)	0.0105	1.1613
C(4)-N(2)	1.123	1.162	1.1487 (16)	0.0121	0.0020	1.1628 (72)	0.0166	1.1652
C(1)-H(1)	0.95		0.997 (23)	0.018	0.002	1.016 (25)	0.024	1.021
C(3)-H(2)	0.98		1.010 (23)	0.018	0.002	1.030 (25)	0.026	1.037

from 1.141 to 1.172 Å (average of four bonds) in a complex of tetracyanoquinodimethane (Hanson, 1968), from 1.141 to 1.17 Å in another such complex (Goldstein, Seff & Trueblood, 1968), and from 1.150 to 1.166 Å in cubic tetracyanoethylene (Little, Pautler & Coppens, 1971), all three structures having been studied at room temperature.

Table 6. *Final bond angles (uncorrected)*

C(3')-C(1)-C(3)	90.02 (4) ^o	C(1')-C(3)-C(1)	89.98 (4) ^o
C(3')-C(1)-C(2)	115.46 (8)	C(1')-C(3)-C(4)	114.53 (8)
C(3)-C(1)-C(2)	115.20 (5)	C(1)-C(3)-C(4)	115.92 (5)
C(3')-C(1)-H(1)	113.9 (5)	C(1')-C(3)-H(2)	114.4 (5)
C(3)-C(1)-H(1)	111.3 (5)	C(1)-C(3)-H(2)	112.0 (5)
C(2)-C(1)-H(1)	109.8 (6)	C(4)-C(3)-H(2)	109.2 (5)
C(1)-C(2)-N(1)	176.82 (7)	C(3)-C(4)-N(2)	178.44 (8)
C(1')...C(1)-C(2)	127.24 (8)	C(3')...C(3)-C(4)	127.05 (8)
C(1')...C(1)-H(1)	122.9 (6)	C(3')...C(3)-H(2)	123.8 (6)

No vibrational corrections have been applied to the bond angles. Their uncorrected values (Table 6 and Fig. 1) are close to those reported by Greenberg & Post (1968). In particular, the slight bending of the C-C≡N legs is confirmed. This departure from linearity tilts the C≡N bonds about 2° more steeply away from the cyclobutane ring plane, but the bending at C(2) has an additional component that turns its C≡N bond 2° towards the adjacent C(4)-N(2) group. The bond angles around the ring atoms show that the bisector of the H-C-C(N) angle is inclined 2° below the ring plane. This may be attributed to asymmetrical hybridization at C(1) or to non-bonded 1-3 interactions with the adjacent ring atoms pressing more strongly on C(2) than on the hydrogen atom.

Deformation density

The charge-density information obtained in this study is embodied in the 36 expansion coefficients from the model *H* refinement, together with the enhanced value of ζ for hydrogen. Direct summation of the several deformation functions pertaining to a complete molecule produces the experimental molecular $\delta\rho$ map shown in Fig. 2. This presents $\delta\rho$ contours in two mutually perpendicular planes, one defined by the cyclobutane ring and one by atoms C(1) and C(2) and the molecular centre of symmetry. The assignment of identical deformation coefficients to chemically equivalent atoms (see above) guarantees that this latter section is essentially identical with the corresponding section through atoms C(3) and C(4).

No inner contours have been drawn within about 0.3 Å of the atomic centres since the calculated values of $\delta\rho$ in these regions are almost entirely without experimental significance. This agrees with the general conclusion of Stewart (1968) about the effect of uncertainty in the vibration amplitudes on the difference density near a first-row nucleus. In most other positions the standard deviations derived from the least-squares covariance matrix are well under 0.1 e Å⁻³,

the interval between adjacent contours. Accordingly, all bond peaks and most of the troughs seen in Fig. 2 may be regarded as experimentally significant in their general appearance if not in their exact positions and detailed shapes.

The cyclobutane ring plane contains four C-C bond peaks centred just outside the square of carbon atoms. The observed offset, about 0.08 Å, from the straight C-C line is perhaps marginally significant but is in good accord with the theoretical prediction of Coulson & Moffitt (1949) as well as with a recent double- ζ calculation on cyclobutane by Kaldor (1973). It also parallels a similar but larger effect observed by Hartman & Hirshfeld (1966) in tricyanocyclopropane. The peak height of 0.41 (2) e Å⁻³ may be compared with a value of 0.3 e Å⁻³ from the double- ζ calculation of Kaldor (1973).

More prominent maxima are found in the substantially shorter exocyclic C-C bond, 0.66 (4) e Å⁻³, and in the C≡N bond, 1.28 (14) e Å⁻³, as well as in the nitrogen lone-pair peak, 1.05 (17) e Å⁻³. Along the C-H bond we find a shoulder of about 0.43 (8) e Å⁻³, which is not quite resolved from the very sharp peak of 2.7 (7) e Å⁻³ at the hydrogen position. The standard deviation assigned to this peak density is hardly better than a guess as it depends critically on the value of ζ_H , which has been estimated by trial and error rather than by least-squares refinement.

Interspersed among the $\delta\rho$ peaks are shallow troughs rarely exceeding -0.2 e Å⁻³ in depth. The disposition of peaks and troughs in the HCCN region seen in Fig. 2(b) closely matches corresponding portions of the theoretical difference densities of HCN and NCCN (Hirshfeld, 1971) as derived from the Hartree-Fock wave functions of McLean & Yoshimine (1967). Thus it appears that the observed deformation density in the vicinity of the C-H, C-C, and C≡N bonds in tetracyanocyclobutane can be approximately simulated by the transfer of the appropriate fragments from these simpler linear molecules. This detailed correspondence, apart from bolstering our trust in the experimental results, supports the general expectation that difference-density features associated with individual chemical groups may often be transferable with little change from one molecule to another.

The positions of the observed maxima and minima around each atomic site conform to a fairly regular pattern that seems to be characteristic of the bonding configuration of the atom. In all atoms, charge accumulates in the bond and lone-pair regions apparently by a process of angular polarization that leaves a more or less continuous envelope of charge depletion in all other directions around the atomic centre. The result is a nearly spherical locus of negative difference density, of mean radius about 0.3 to 0.7 Å and maximum depth about -0.2 e Å⁻³, traversed by a small number of broad spokes of excess density in the bonding and lone-pair directions. Thus, the hydrogen atom, forming just one bond peak, shows a dipolar pattern of angular

polarization superimposed on pronounced radial contraction and is accordingly surrounded almost completely by a very diffuse envelope of negative $\delta\rho$, which has lost charge both to the bond peak and to the sharp cusp density around the nucleus. In analogous manner, the digonally hybridized cyano atoms C(2) and N are each surrounded by a broad electron-deficient equatorial band from which charge has migrated towards the two poles to produce a pair of stubby peaks opposite one another on the bond axis. Similarly, the tetrahedral array of bond peaks around the tetravalent carbon atom C(1) is mirrored by a corresponding array of shallow troughs localized approximately opposite the bonds. The analogous pattern around a trigonally hybridized atom would comprise a pair of charge-depleted polar caps, on either side of the bonding plane, linked together by three riblike troughs that cross this plane in the sectors opposite a triangular array of bond peaks. Approximations to this idealized pattern are commonly observed, as in the carbon and nitrogen atoms of cyanuric acid (Verschoor & Keulen, 1971) and fumaramic acid (Hirshfeld, 1971).

It is customary to try to condense a molecular charge distribution, whether experimental or theoretical, into a compact list of numerical indices, such as atom populations, bond orders and the like. The numerical quantities most naturally related to our deformation model are the net charges and dipole moments localized on the several atoms. These are obtained directly by summation of the coefficients of the even and the odd deformation functions, respectively, on each atomic centre. The atomic charges and moments so derived from model *H* are presented in Fig. 3, with the usual warning about the essential arbitrariness of all such numerical measures. Comparison of the results from models *E*, *G* and *H* may help to underline this warning. These three refinements are very similar in most respects, including the detailed appearance of the respective $\delta\rho$ maps, yet produce calculated atomic charges differing by as much as 0.18 e and atomic moments differing by up to 0.22 D. The differences, however, are nicely correlated in that any change in the polarity of a bond is nearly balanced by opposing changes in the moments on its two atoms. Accordingly we may expect these numerical data to yield a fair account of the gross distribution of charge within the molecule and, thereby, of the electrostatic field that it presents to the outside world.

The C-H bond appears, from the atomic charges at its two ends, to be highly polar. But this charge separation, representing an apparent moment (referred to the bond midpoint) of 1.56 D in the sense $\overset{-}{\text{C}}-\overset{+}{\text{H}}$, is largely offset by the atomic moments on C and H, which together yield an opposing moment of 1.01 D. On the other hand, the polarity of the C \equiv N bond, amounting to 0.52 D, is augmented by the atomic moment on C(2) so that the cyano group as a whole may be assigned a net moment of 1.04 D in the expected sense $\overset{+}{\text{C}}\equiv\overset{-}{\text{N}}$. One

evident consequence of this overall pattern of charge displacements is that the closest intermolecular contacts in the crystal (Greenberg & Post, 1968) bring together a positively charged hydrogen atom of one

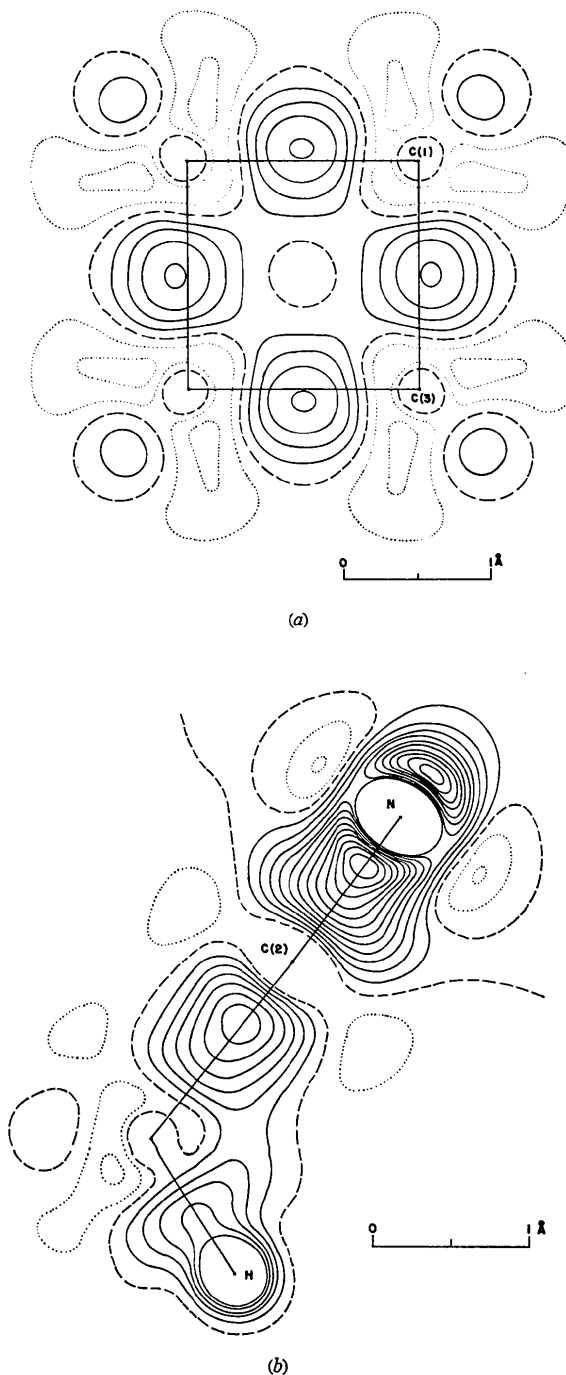


Fig. 2. Molecular deformation density. Contour interval $0.1 \text{ e } \text{Å}^{-3}$; zero contour broken, negative contours dotted. Inner contours around atomic centres have been omitted. (a) Cyclobutane ring plane. (b) HCCN plane.

molecule and a negatively charged nitrogen of its neighbour.

The atomic moments shown in Fig. 3 imply a dipolar asymmetry of charge around each atomic centre that can be correlated with shifts in the apparent positions of the atoms when these are assumed spherical, as in model *B*. Such shifts are often found in comparisons of X-ray and neutron-diffraction data for the same crystal structure (Coppens & Hirshfeld, 1964; Coppens & Vos, 1971). In our case we can compare atomic positions derived from models *B* and *H*, supposing the latter to provide true nuclear positions such as would be revealed by neutron diffraction. When the charge asphericity is neglected, atoms C(2) and C(4) move 0.005 Å into the respective C≡N bond regions. This shift accords with the large atomic moment on C(2), reflecting the evident asymmetry in charge distribution between the relatively electron-poor C–C bond on one side and the electron-rich C≡N bond on the other. The nitrogen atom, though having according to Fig. 3 a negligible atomic moment, is displaced in model *B* 0.003 Å into the C≡N bond. This behaviour probably reflects a delicate balance between the very compact lone-pair charge concentration on one side of the atom and the triple-bond charge on the opposite side. The indicated atomic displacements in model *B* have the net effect of shortening the C≡N bond by 0.008 Å relative to model *H*. If such shortening is a general phenomenon it may be a further reason for the short C≡N bond lengths commonly revealed by X-ray diffraction (see above).

The hydrogen atoms are displaced, in model *B*, 0.04 Å towards the adjacent carbon atoms. This familiar behaviour is in accord with the net polarity of the C–H

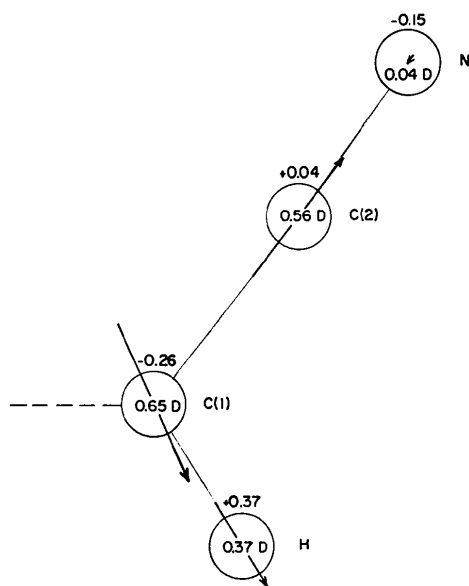


Fig. 3. Atomic charges (above circles) and dipole moments (arrows).

bond but not with the hydrogen atomic moment, which is directed, unexpectedly, in the opposite sense. The ring atoms C(1) and C(3) move only 0.001 Å, in no particular direction, suggesting that the large atomic moment at this position is something of an artifact, whose real function, like that of the anomalous moment on hydrogen, may be to correct the excessive polarity of the C–H bond.

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The Crystal Structure of Lead(II) Thiocyanate

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The title compound has four $\text{Pb}(\text{NCS})_2$ units in a cell with $a=9.661$, $b=6.544$, $c=8.253$ Å and $\beta=92.37^\circ$, belonging to the space group $C2/c$. The structure has been refined to $R=4.7\%$ for 974 Mo data. The lead atom lies on a twofold axis and is environed by four nitrogen and four sulphur atoms. The NCS unit has $\text{N}-\text{C}=1.172$ (10), $\text{C}-\text{S}=1.639$ (8) Å, and $\text{N}-\text{C}-\text{S}=178.6$ (8)°; it makes contacts with four Pb atoms via two $\text{Pb}-\text{N}$ [2.687 (7), 2.781 (7) Å] and two $\text{Pb}-\text{S}$ [2.996 (2), 3.135 (2) Å] bonds.

Introduction

Some years ago we reported (Mokuolu & Speakman, 1966) the crystal structure of lead thiocyanate. The results were of low accuracy, as they were based on limited data with copper radiation, and only crudely corrected for absorption which was high. We now report a more precise determination.

Experimental

Lead thiocyanate was prepared by a standard method. Good crystals are easily grown by slowly cooling a saturated solution in hot water. They develop a yellowish cast and are said to be sensitive to light, but they seem to be very stable to X-rays. The counts from standard reflexions did not change significantly over long periods. The following crystal data were established from diffractometer measurements with Mo $K\alpha$ radiation ($\lambda=0.71069$ Å): $\text{Pb}(\text{NCS})_2$, $M=323.4$, monoclinic, $a=9.661 \pm 0.004$, $b=6.544 \pm 0.003$, $c=8.253 \pm 0.003$ Å, $\beta=92.37 \pm 0.02^\circ$, $U=521.3$ Å³, $Z=4$, $D_m=4.082$ g cm⁻³ [Huttner & Knappe, 1930; the value of 3.82 cited in Groth (1908) originated from Schabus (1850)], $D_c=4.12$ g cm⁻³, absorption coefficient (Mo $K\alpha$) $\mu=316$ cm⁻¹. Space group $C2/c$ or Cc : absences, hkl when $h+k$ odd; $h0l$ when either h or l odd; $0k0$ when k odd. The former (No. 15) was

adopted because the goniometric evidence indicates the point group $2/m$, and the choice was vindicated by the analysis. The lead atom must lie in a special position, and the two thiocyanate groups are equivalent.

Operation of the transformation matrix $0, 0, -\frac{1}{2}/0, 1, 0/-1, 0, \frac{1}{2}$ converts the cell defined above to one with $a'=4.1265$, $b'=6.544$, $c'=10.661$ Å, $\beta'=115.12^\circ$. The agreement between the ratios corresponding to this pseudo-cell and those given by Groth is impressive evidence of the accuracy of the goniometric method when applied to good crystals:

Goniometric	0.6310:	1:	1.6288;	$115^\circ 6\frac{1}{2}'$
Diffractometer	0.6306:	1:	1.6291;	$115^\circ 7'$

Intensities were measured on a Hilger-Watts four-circle diffractometer, with a graphite monochromator and Mo $K\alpha$ radiation, the $\omega-2\theta$ scan being used. The crystal had dimensions $0.21 \times 0.11 \times 0.25$ mm and was mounted about $[1\bar{1}0]$. To apply absorption corrections (by *ABSORB* from the University of Maryland's X-RAY 72 System), the shape of this crystal was defined by 13 faces, each with its normal distance from a point near the centre. Transmission factors for intensities ranged from 0.025 to 0.100. Two sets of data were collected: (I) with θ out to 25° , and (II) from 25 to 34° . The other usual corrections were applied and standard deviations assessed by the formula, $\sigma^2(I) = C + (T_p/T_B)^2(B_1 + B_2) + 0.04 I^2$, where I is the derived intensity, C the integrated peak count over time T_p , and B_1, B_2 are the two background counts over time T_B .

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