CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
CRUICKSHANK, D. W. J. *et al.* (1961). *Computing Methods and the Phase Problem in X-Ray Crystal Analysis,* Paper 6. Oxford: Pergamon Press.
FERRARIS, G. (1965). *Atti Accad. Torino,* **99**, 457.
FERRARIS, G. & FORMIA, F. (1965). To be published.
FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.
FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee: General Electric Company.
HAMILTON, W. C. (1961). *Acta Cryst.* **14**, 95.
HODGKIN, D. C. & PITT, G. J. (1950). *Rep. Progr. Chem.* **47**, 457.
MERRITT, L. L. & LANTERMAN, E. (1952). *Acta Cryst.* **5**, 811.
MILONE, M. & BORELLO, E. (1957). *Nuovo Cim.* [*Ser.* 10] **5**, 562.
MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
NAKAMOTO, K., MARGOSHES, M. & RUNDLE, R. E. (1955). *J. Amer. Chem. Soc.* **77**, 6480.
PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
ROLLETT, J. J. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.
TEMPLETON, D. H. (1959). *Acta Cryst.* **12**, 771.
WITTEMBERG, M. & MEYER, V. (1883). *Ber. dtsch. chem. Ges.* **16**, 505.

Acta Cryst. (1966). **20**, 80

Structure of *cis*-1,2,3-Tricyanocyclopropane

BY A. HARTMAN AND F. L. HIRSHFELD,

Department of X-ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel

(*Received* 17 *May* 1965)

A three-dimensional X-ray diffractometric study of $(CHCN)_3$, space group $R3c$, yields an endocyclic bond length (1·518 Å) and adjacent angles virtually duplicating those in cyclopropyl chloride. Other bond lengths are: exocyclic C–C, 1·449 Å, C≡N, 1·144 Å; these two bonds make an angle of 178·1°. The molecule departs slightly from $3m$ symmetry because of close N · · · H and N · · · C contacts in the crystal.

The difference electron density has a peak of $+0{\cdot}06$ e.Å^{-3} at the midpoint of the exocyclic C–C bond and one of $+0{\cdot}05$ e.Å^{-3} displaced 0·32 Å in the expected direction from the axis of the endocyclic bond. At the midpoint of the C≡N bond is a trough of $-0{\cdot}03$ 3.Å^{-3}.

In preparation for the study, by X-ray diffraction at low temperature, of the electron-density distributions in small organic molecules, we have determined, at room temperature (26° ± 1 °C), the crystal structure of *cis*-1,2,3-tricyanocylopropane $(CHCN)_3$ (Sadeh & Berger, 1958; Griffin & Peterson, 1963). The space group is $R3c$ and the hexagonal unit cell, with dimensions $a = 9{\cdot}8815 \pm 0{\cdot}0020$ Å and $c = 10{\cdot}4185 \pm 0{\cdot}0012$ Å (based on $\lambda = 1{\cdot}54050$ Å for Cu $K\alpha_1$), contains six molecules; $d_{\text{calc}} = 1{\cdot}324$. The molecule lies on a threefold rotation axis and the asymmetric unit comprises four atoms in general positions.

The crystal grows from aqueous ethanol as thin needles, elongated along the polar c axis. Cutting with a stream of abrasive powder (Pepinsky, 1953) yielded a hexagonal prism whose largest dimension was 0·5 mm. The reflexion intensities were measured with nickel-filtered Cu $K\alpha$ radiation on a General Electric single-crystal orienter (Furnas, 1957) with stationary crystal and counter and a 10° take-off angle, which provided a convergent beam 0·6° wide at the crystal. At low and medium Bragg angles ($2\theta < 130°$) the α_1–α_2 doublet was recorded; at higher angles the α_1 component alone was recorded, with the counter aperture set to exclude the α_2 reflexion. Of the 225 independent reflections accessible within the instrumental range of $2\theta < 165°$, one – 550 – gave no detectable intensity above a rather high background, due to Fe $K\alpha$ contamination, and was treated as unobserved but with low statistical weight and high threshold value; a second – 0,5,10 – could not be properly measured because of this same contamination and was given zero weight.

The measured intensities were corrected for absorption (Coppens, Leiserowitz & Rabinovich, 1965) and, towards the end of the refinement, for extinction (Zachariasen, 1963) with a computer program written by Mr L. Leiserowitz. The absorption factor varied between 0·76 and 0·84; the largest extinction correction amounted to 13% of the observed intensity. Comparison of the absorption-corrected intensities of sixteen pairs of symmetry-related reflexions led to an estimated random error in intensity of about 1·1% superimposed on the statistical counting error, *i.e.*

$$\sigma^2(F_o^2) \sim K^2(I+B+2)/10 + (0{\cdot}011\ F_o^2)^2\,,$$

where I and B are the reflexion and background counts, respectively, after reduction by an invisible first decade scaler, and $K = F_o^2/(I-B)$ includes scaling, Lorentz, polarization, absorption, and extinction corrections. The estimated standard deviations of the stronger reflexions were increased above this estimate to allow for a 10% uncertainty in the extinction correction.

Solution of the structure amounted to estimating the azimuthal orientation of the molecule about its threefold symmetry axis. Packing considerations established this parameter to within 10°. The scale factor and the positional coordinates and anisotropic thermal parameters of the four atoms were subjected to full-matrix least-squares refinement on a Control Data Corporation 1604-A computer, with a modified version (Coppens & Hirshfeld, unpublished) of the Busing & Levy (1962) FORTRAN program that minimizes r, defined below. Atomic scattering factors for C and N were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); for hydrogen the theoretical free-atom curve was adjusted to an effective nuclear charge of 1·2, as suggested by current work on 2,5-dimethyl-*p*-benzoquinone (Hirshfeld & Rabinovich, to be published). Final discrepancy indices are

$$R=\Sigma\big|kF_o-|F_c|\big|/\Sigma kF_o=0{\cdot}023\,,$$

$$r=\Sigma w(k^2F_o^2-|F_c|^2)^2/\Sigma wk^4F_o^4=0{\cdot}0032\,.$$

The weighting factors w were defined by

$$1/w=\sigma^2(F_o^2)+4a^2F_o^2/k^2\,,$$

in which $\sigma(F_o^2)$ is the experimental uncertainty, discussed above, and a, an assumed r.m.s. error in $|F_c|$ due to deficiencies of the model (approximate f curves, neglect of bond densities, etc.), was estimated at $a=0{\cdot}084$ (with F_c computed for the two-molecule primitive unit cell) from the intercept of a plot of $(kF_o-|F_c|)^2$ *vs* $\sigma^2(F_o)=\sigma^2(F_o^2)/4F_o^2$.

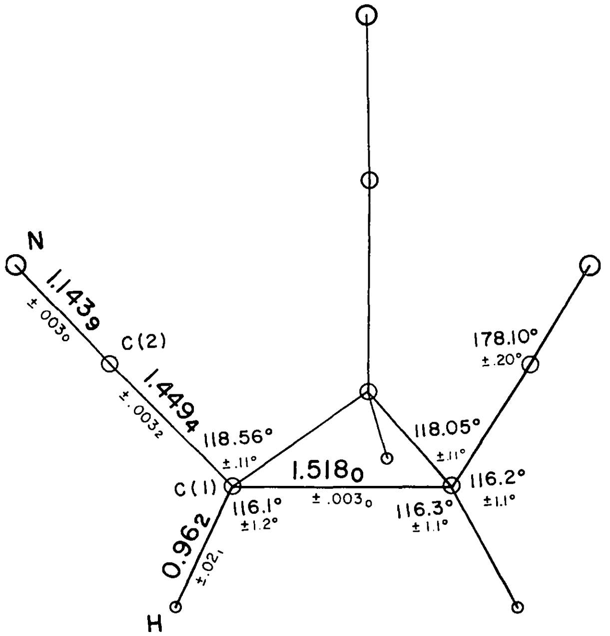

Fig. 1. Molecular dimensions, corrected for libration, and their estimated standard deviations.

The experimental mean square vibration amplitudes of the carbon and nitrogen atoms, whose estimated standard deviations are mostly smaller than 0·001 Å^2, were used to determine, by least squares, the molecular rigid-body vibration tensors (Cruickshank, 1956). This treatment led to r.m.s. translation amplitudes of 0·18 Å along **c**, 0·21 Å perpendicular to **c**, and r.m.s. libration amplitudes of 1·7° about **c**, 4·8° about axes perpendicular to **c** and passing roughly midway between the nitrogen and hydrogen ends of the molecule. Residual discrepancies up to 0·01 Å^2 between the experimental atomic vibration components U^{ij} and those attributable to rigid-body motion do not appear to be interpretable as internal vibration and raise a suspicion of unidentified systematic errors.

Atomic coordinates (Table 1) were corrected for molecular libration on the assumption that the experimental positions define the centroids of the charge clouds. Estimated standard deviations of the corrected lengths and angles (Fig. 1) include a postulated 25% standard deviation in the libration corrections, superimposed on the experimental errors deduced from the covariances of the atomic coordinates.

The endocyclic C–C bond length and all adjacent bond angles are virtually identical with the corresponding dimensions in cyclopropyl chloride, as revealed by microwave spectroscopy (Schwendeman, Jacobs & Krigas, 1964). The exocyclic C–C bond length is appropriately intermediate between the values characteristic for an $sp-sp^2$ and an $sp-sp^3$ bond (see, *e.g.* Stoicheff, 1962); the C≡N bond is distinctly shorter than, for example, those studied by Costain (1958) and by Costain & Stoicheff (1959).

The difference electron density in the plane of the cyclopropane ring (Fig. 2) shows a peak of +0·05 e.Å^{-3}, attributable to bonding density, displaced 0·32 Å from the axis of the highly strained endocyclic bond. The line joining this peak to each of the adjacent carbon atoms makes an angle of 22° with the C–C interatomic vector; Coulson & Moffitt (1949) calculated that the axis of the bond orbital in cyclopropane should be inclined 22° to the internuclear line. The exocyclic C(1)–C(2) bond has a similar peak of $\Delta\varrho=+0{\cdot}06$ e.Å^{-3} centred just at its midpoint. The midpoint of the C≡N bond is marked by an unexpected trough of $-0{\cdot}03$ e.Å^{-3}; this may be related to the negative theor-

Table 1. *Atomic coordinates*

	Uncorrected						Corrected		
	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	x	y	z
H	0·1300	0·0024	−0·0143	0·0024	−0·0789	0·0019	0·1306	−0·0144	−0·0800
C(1)	0·08323	0·00018	−0·00947	0·00019	0	0	0·08356	−0·00950	−0·00053
C(2)	0·15935	0·00019	−0·01672	0·00019	0·11560	0·00023	0·15998	−0·01679	0·11588
N	0·21790	0·00021	−0·02011	0·00019	0·20854	0·00019	0·21875	−0·02019	0·20946

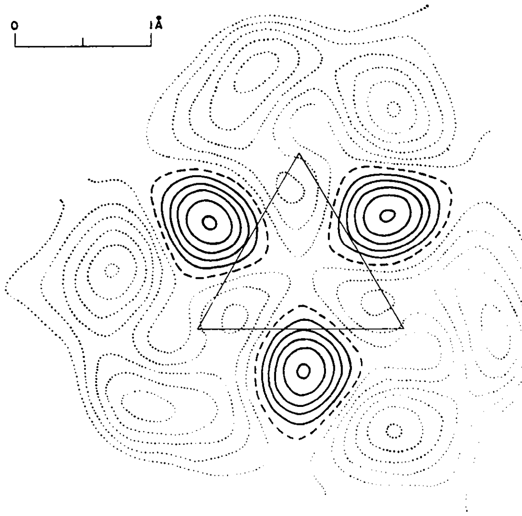

Fig. 2. Difference density in plane of cyclopropane ring. Contour interval 0·01 e.Å^{-3}, zero contour broken. Estimated standard deviation averages 0.017 e.Å^{-3}.

etical difference density that self-consistent-field calculations (Scherr, 1955) place along the bond axis in the N_2 molecule (Bratož, Daudel, Roux & Allavena, 1960).

Intermolecular N · · · H contacts of 2·73 and 2·81 Å and N · · · C(2) contacts of 3·10 Å hold the structure firmly together and lead to small departures, up to 0·015 Å, from $3m$ molecular symmetry. An interesting, though expected, feature is the non-linearity of the C–C≡N angle; the C≡N bond is deflected 1·7° towards the molecular symmetry axis. While an intermolecular source cannot be ruled out, the deflection is thought to reflect a bending of the C(1)–C(2) bond, with consequent rotation of the C(2) valence orbitals (Hirshfeld, 1964), as a result of repulsion between C(2) and H.

We are grateful to Professor G. W. Griffin and to Dr T. Sadeh for samples of the compound.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Bratoz, S., Daudel, R., Roux, M. & Allavena, M. (1960). *Rev. Mod. Phys.* **32**, 412.

Busing, W. R. & Levy, H. A. (1962). ORFLS Least-squares Program. I.U.Cr. *World List of Crystallographic Computer Programs,* No. 360.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035.

Costain, C. C. (1958). *J. Chem. Phys.* **29**, 864.

Costain, C. C. & Stoicheff, B. P. (1959). *J. Chem. Phys.* **30**, 777.

Coulson, C. A. & Moffitt, W. E. (1949). *Phil. Mag.* **40**, 1.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Furnas, T. C. (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee: General Electric Co.

Griffin, G. W. & Peterson, L. I. (1963). *J. Org. Chem.* **28**, 3219.

Hirshfeld, F. L. (1964). *Israel J. Chem.* **2**, 87.

Pepinsky, R. (1953). *Rev. Sci. Instrum.* **24**, 403.

Sadeh, T. & Berger, A. (1958). *Bull. Res. Council Israel,* 7A, 98.

Scherr, C. W. (1955). *J. Chem. Phys.* **23**, 569.

Schwendeman, R. H., Jacobs, G. D. & Krigas, T. M. (1964). *J. Chem. Phys.* **40**, 1022.

Stoicheff, B. P. (1962). *Tetrahedron,* **17**, 135.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1966). **20**, 82

The Extension of the Isomorphous Replacement Method to Include Anomalous Scattering Measurements

By B. W. Matthews

Medical Research Council Laboratory of Molecular Biology, Hills Road, Cambridge, England

(*Received* 3 *May* 1965)

The combination of isomorphous replacement and anomalous scattering data in phase determination of non-centrosymmetric reflexions is discussed. Expressions are derived which take into account the relative reliabilities of the experimental observations and enable any combination of replacement atoms to be used in the phase determination.

North (1965) has proposed an improved method for the combination of isomorphous replacement and anomalous scattering data in phase determination of non-centrosymmetric reflexions which makes use of the greater intrinsic accuracy of the anomalous scattering measurements. North's formulation leads to alternative expressions for the phase probability distribution, and North leaves it open as to which of these expressions should be used in practice. The purpose of this communication is to show that the problem may be exam-