The Crystal and Molecular Structure of 1,1,2,2-Tetracyanocyclopropane

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A detailed analysis of the crystal structure of 1,1,2,2-tetracyanocyclopropane is reported and the results are critically compared with a previous study. The compound crystallizes in space group $P2_12_12_1$ with $a = 6\cdot202(1)$, $b = 6\cdot918(2)$ and $c = 16\cdot130(4)$ Å. The pattern of ring bond lengths derived is consistent with an analysis of possible interactions of certain Walsh orbitals of cyclopropane with π-acceptor substituents such as C≡N. In particular, the C(1)–C(2) bond is lengthened to a value of $1\cdot563$ Å after libration corrections. Effects due to inadequate modeling of the real electron density by the use of spherically symmetric scattering factors on the apparent bond lengths were minimized in an extended analysis by using only data with $(\sin\theta/\lambda_{\text{Mo} K\alpha}) \geq 0\cdot478$ in the final refinements. Rigid-body libration corrections were analyzed for all bond lengths and subsequent riding corrections, based on residual thermal parameters, were applied to the C–N bonds.

Introduction

The Walsh (1947, 1949) analysis of bonding in cyclopropane has provided a useful model for the interpretation of the effects of substituents on ring geometry (Günther, 1970; Hoffmann, 1970, 1971*a*; Hoffmann & Stohrer, 1971). Specifically, a π-donor substituent is expected to populate a vacant symmetric antibonding orbital of cyclopropane and weaken all ring bonds. In contrast, the low-lying unoccupied orbitals of π-acceptor substituents can interact with the antisymmetric component of the doubly degenerate higher bonding orbital of cyclopropane; such an interaction would weaken the vicinal ring bonds and strengthen the distal ring bond (Hoffmann, 1971*a*).

The bonding patterns of a number of cyclopropane derivatives (Peterson, 1956; Grant & Speakman, 1958; Long, Sparks & Trueblood, 1965; Fritchie, 1966; Meester, Schenk & MacGillavry, 1971; Heller, Dreiding, Grieb & Niggli, 1972; Luhan & McPhail, 1972) are consistent with this interpretation. We undertook a study of 1,1,2,2-tetracyanocyclopropane (TCCP) to examine the cumulative effects of four strong π-acceptor substituents. An analysis by Hoffmann (1971*a*, *b*) suggests that, in this compound, the C(1)–C(3) and C(2)–C(3) bond lengths should approximately equal those in unsubstituted cyclopropane, and that the C(1)–C(2) bond should be significantly longer. Our structure analysis completely confirmed this prediction (Lemley, 1972) as did the results of an independent investigation (Wang & Stucky, 1973) that appeared shortly after this structure was completed. This report is presented because our study differs from that of Wang & Stucky in several important respects:

(i) We were able to record a very much larger number of diffraction data.

(ii) This made it possible to undertake extensive rigid-body thermal libration analyses and to apply subsequent riding corrections both of which resulted in significant corrections to the bond parameters.

(iii) It also made it possible to systematically exclude low-angle data from least-squares refinement and thereby minimize errors introduced by the inadequate representation of asymmetric electron density distributions by spherically symmetric atomic scattering factors.

This latter procedure resulted in significant corrections to bond parameters in part because of the high percentage of the atoms in TCCP that display large deviations from spherical symmetry in the bonding electron distributions. Thus, the molecule is an excellent test case for consideration of wider application of this technique.

Finally, it should be noted that the molecule TCCP is of considerable interest as a model system for quantum mechanical calculations; thus, it is appropriate that well-corrected and accurate bond parameters be available.

Experimental

A sample of TCCP (Scribner, Sausen & Prichard, 1960) was obtained from Dr W. W. Prichard‡ through the intermediary, Dr R. Hoffmann; the crystal used in the analysis had dimensions $0\cdot3 \times 0\cdot3 \times 0\cdot4$ mm and the measured density was $\varrho_{\text{obs}} = 1\cdot35$ g cm^{-3}. The diffraction symmetry and systematic absences uniquely indicated the space group $P2_12_12_1$ with $a = 6\cdot202$ (1), $b = 6\cdot918$ (2), $c = 16\cdot130$ (4) Å, $Z = 4$ and $\varrho_{\text{calc}} = 1\cdot364$ g cm^{-3}. Diffraction intensities were measured with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å) to $\sin\theta/\lambda = 0\cdot817$ Å^{-1} on a Picker FACS-1 diffractometer operated

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in the θ–2θ scan mode. The scan rate was $1°$ min^{-1} in 2θ and the scan range included a variable increment in angle above the minimum ($1.3°$ at $2\theta = 0$) to allow for spectral dispersion. Background counts of 40 s duration were measured at each end of the scan. Of a total of 1868 reflections investigated, 1766 were statistically observable by the criterion $F_o \geq 1.4\sigma_F$, where the observed structure factor (F_o) and its standard deviation (σ_F) are defined as

$$F_o = [(C - kB)/\text{Lp}]^{1/2} ,$$
$$\sigma_F = (C + k^2 B)^{1/2}/(2F_o\text{Lp}) .$$

In these expressions C and B represent total scan counts and background counts respectively, and k is the ratio of scan time to total background count time. Corrections were made for Lorentz and polarization effects and, in the final refinement of all 1766 reflections, for secondary extinction (Zachariasen, 1968).

Solution and refinement

The structure was solved by direct methods (Karle & Karle, 1966) using a computerized (Tsai, 1971) multiformula procedure based upon square-tangent (Haupt-

man, 1970) and generalized product relationships (Tsai & Collins, 1972). An E synthesis of 180 data with statistically acceptable phases clearly defined nine atomic positions. The remainder of the structure emerged in a subsequent difference Fourier synthesis.

Refinement was effected by full-matrix least-squares (Busing, Martin & Levy, 1962) analysis of positional and anisotropic thermal parameters for carbon and nitrogen atoms, a scale factor, and an extinction parameter; hydrogen atom positions from difference syntheses were included but not refined. The refinement converged with the full data set to yield a standard residual $R = 0.048$ and a weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.052$, wherein $w = 1/\sigma_F^2$ and $\sigma_F = \sum_{n=0}^{3} a_n|F_o|^n$. The coefficients a_n were obtained from a least-squares minimization of $||F_o| - |F_c||$ with the functional form $\sum_{n=0}^{3} a_n|F_o|^n$ over all data used in the refinement.

It is clear that the distribution of electrons in the cyano groups and in the three-membered ring of this molecule cannot be represented accurately by normal atomic scattering factors. Parameterizing the electron
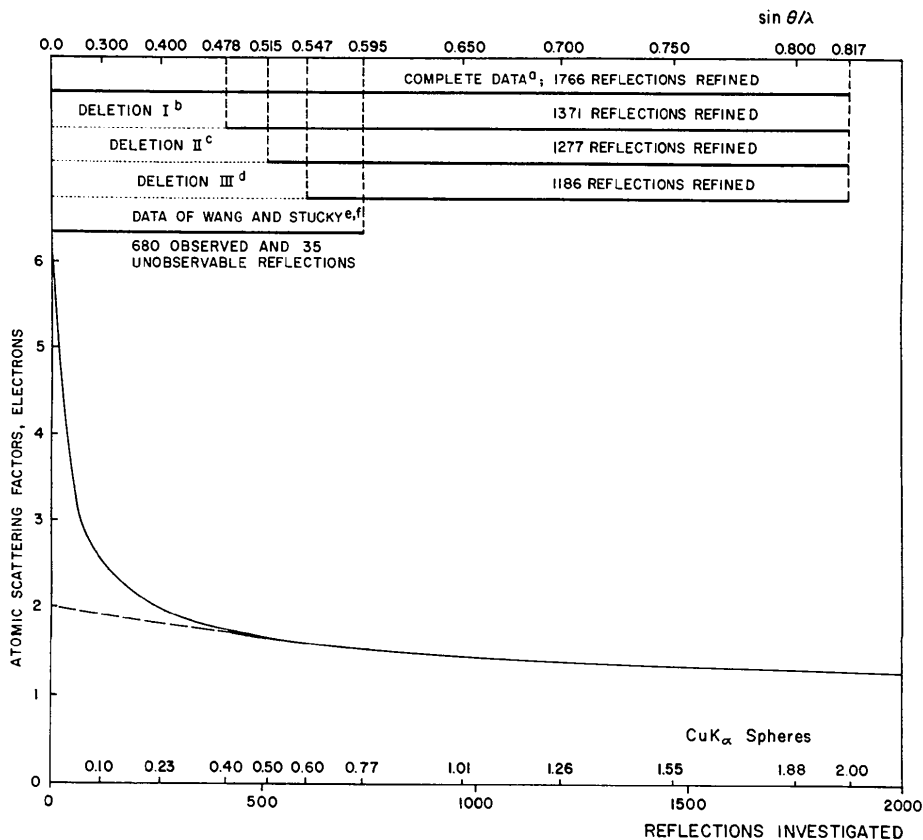

Fig. 1. The atomic scattering factor for carbon and the ranges of data used in the five refinements of interest. See text for explanation. (a) Two Cu $K\alpha$ spheres investigated; 1766 observable reflections of 1868 non-extinct reflections measured. (b) Deletion of 395 reflections observed in first 0.4 Cu $K\alpha$ sphere. (c) Deletion of 489 reflections observed in first 0.5 Cu $K\alpha$ sphere. (d) Deletion of 580 reflections observed in first 0.6 Cu $K\alpha$ sphere. (e) 715 reflections investigated correspond to 0.77 Cu $K\alpha$ sphere. (f) See Wang & Stucky (1973).

density heavily concentrated along the C–N bond solely by partial superposition of spherically symmetric form factors results in an apparent foreshortening of the bond length. To minimize this effect, an extended analysis was undertaken in which first, all data contained within the volume of the inner 0·4 (sin $\theta/\lambda_{Mo\,K\alpha} <$ 0·478) Cu $K\alpha$ sphere and subsequently, within the inner 0·5 (sin $\theta/\lambda_{Mo\,K\alpha} < 0·515$) and 0·6 (sin $\theta/\lambda_{Mo\,K\alpha} < 0·547$) Cu $K\alpha$ spheres, were excluded from the final refinement process.

In Fig. 1, the atomic scattering factor for carbon is plotted against a linear scale of the number of reflections investigated. Corresponding values of sin $\theta/\lambda_{Mo\,K\alpha}$ are also indicated along with a linear scale in units of a full Cu $K\alpha$ sphere of data. In addition, bar graphs are presented for the five refinements of interest; in each case, the number of statistically observable data is indicated for the range of sin $\theta/\lambda_{Mo\,K\alpha}$ measured. It can be seen that the final deletion of 0·6 Cu $K\alpha$ sphere of data eliminated most of the reflections used by Wang & Stucky (1973) but still maintained a data-to-parameter ratio of 11·7 as compared to 6·7 in their analysis.

Following complete refinement of the full data set, each of the truncated refinements converged satisfactorily. All positional parameters were found to be invariant, within a standard deviation, to further deletion of data beyond the inner 0·4 Cu $K\alpha$ sphere (sin $\theta/\lambda_{Mo\,K\alpha} < 0·478$). Nevertheless, with respect to the refinement of the full data set, the variations were very significant. In accord with our expectations, these changes resulted in significant increases in the C–N bond lengths. This clearly indicates that the influence of the inadequate parameterization of the bonding electrons is reduced, when the core data are removed from the refinement.

Thus, the refinement with 1371 reflections (sin $\theta/\lambda_{Mo\,K\alpha} \geq 0·478$) is deemed to provide the most accurate bond parameters, although it might be expected that the thermal parameters would be less reliable. With a final data-to-parameter ratio of 13·7, this refinement converged with $R=0·055$ and $R_w=0·054$. Although extinction corrections applied to the full data set were significant at low angles, the effects on the truncated data set were negligible.*

Corrections to the bond lengths for thermal motion were calculated for several models. A rigid-body least-squares analysis (Trueblood, 1968) of the anisotropic thermal parameters of all non-hydrogen atoms, based on the data set truncated at sin $\theta/\lambda=0·478$, indicated the need for uniform increments of 0·005 and 0·002 Å to all C–C and C–N bonds respectively. Expected anis-

otropic thermal parameters based upon the rigid-body motion parameters were then calculated for each atom. These were subtracted from the experimentally determined thermal parameters to yield (positive definite) residual thermal parameters. Subsequent riding corrections (Busing & Levy, 1964) based upon these residual thermal parameters (Johnson, 1970) were negligible for C(ring)–C(cyano) bonds and variable for the C–N bonds over a range 0·002–0·008 Å (mean value 0·004 Å). The sum of these two corrections is somewhat less than might be expected (Little, Pautler & Coppens, 1971) considering the magnitude of the thermal parameters.

In another analysis, later deemed to be the most acceptable, rigid-body parameters were determined from the anisotropic thermal parameters of the seven carbon atoms only; calculated increments were 0·004 Å for C(ring)–C(ring) bonds, 0·003 Å for C(ring)–C(cyano) bonds and 0·002 Å for C–N bonds. The corresponding riding corrections based, as before, on the residual thermal parameters gave increments of 0·001 Å for C(ring)–C(cyano) bonds and variable corrections for the C–N bonds, ranging from 0·007 to 0·014 Å with a mean value of 0·009 Å (e.s.d. =0·003 Å).

For the purposes of comparison, riding corrections to C–N bonds were calculated directly from the thermal parameters uncorrected for rigid-body motion. These followed the same pattern but gave unreasonably high values that ranged from 0·016 to 0·027 Å with a mean value of 0·020 Å (e.s.d. =0·005 Å). Other rigid-body decompositions were undertaken but they did not provide any further insights into the vibrational analysis problem.

Similar calculations were made based on thermal parameters derived from the full data set; the calculated corrections were nearly identical in all cases, despite the fact that the uncorrected bond lengths were substantially different. This eliminates any possible questions about the use of thermal parameters derived from the truncated data set in the analysis of the rigid-body motion of the molecule. Nevertheless, it should be remarked that with the full data set, the distortions imposed upon the molecular geometry by the inadequacies of the spherically symmetric scattering factors are also resident in the associated thermal parameters. We judge that the thermal motions of the atoms are better represented in the analysis of the truncated data set; despite the diffraction effects that invariably must occur because of the missing terms, the residual Fourier density should more nearly reflect the true anisotropies in the distributions of the core electrons in the atoms.

Results and discussion

Final atomic positional parameters and anisotropic thermal parameters based on the data set with (sin $\theta/\lambda) \geq 0·478$ Å^{-1} appear in Tables 1 and 2 respectively. A comparison of several bond length and bond angle

calculations is provided in Table 3.* Uncorrected values are given for both the complete and truncated data set analyses; corrected values are listed only for the latter. We note that the uncorrected bond parameters derived from our complete data set are virtually identical with the corresponding values of Wang & Stucky (1973) that were derived from a very much smaller data set.

Corrections derived from the rigid-body analysis are listed separately in Table 3; the total corrections include a term for riding motion as well. Both the rigid-body and the subsequent riding-motion analyses were based upon the assumption of the seven-atom carbon unit as the basic rigid element in the structure. No standard deviations are explicitly attached to bond parameters corrected for thermal motion. We believe that a conservative estimate of the standard deviations

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* Estimated standard deviations in each table were calculated using the program *ORFFE* (Busing, Martin & Levy, 1964). Standard deviations of the lattice constants were included.

for the corrected values should be at least twice those for the uncorrected values. Fig. 2 provides a labeled perspective view of the molecule on which the fully corrected and the uncorrected molecular dimensions are recorded.

Table 1. *Final atomic fractional coordinates* ($\times 10^4$)

The estimated standard deviations in parentheses apply to the last significant digit. All values are derived from data with $(\sin \theta/\lambda_{Mo\,K\alpha}) \geq 0.478$ Å^{-1}.

	x	y	z
C(1)	7850 (2)	5912 (2)	1580 (1)
C(2)	7632 (2)	4903 (2)	720 (1)
C(3)	8916 (2)	3980 (2)	1412 (1)
C(4)	5934 (3)	5959 (2)	2089 (1)
C(5)	9133 (3)	7658 (3)	1608 (1)
C(6)	5529 (2)	4134 (2)	528 (1)
C(7)	8791 (2)	5783 (2)	420 (1)
N(1)	4397 (5)	5987 (4)	2487 (2)
N(2)	10137 (4)	9053 (3)	1633 (2)
N(3)	3832 (3)	3525 (3)	408 (2)
N(4)	9782 (3)	6499 (3)	-474 (1)
H(1)	8219	2836	1682
H(2)	10518	4012	1341

Table 2. *Thermal parameters* (Å^2)

The estimated standard deviations in parentheses apply to the last significant digit. The anisotropic B_{ij} (Å^2) are related to the dimensionless β_{ij} employed during the least-squares refinement, by $B_{ij}=4\beta_{ij}/a_i^*a_j^*$; where β_{ij} is given by the expression: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. All values are derived from refinement of data with $(\sin \theta/\lambda_{Mo\,K\alpha}) \geq 0.478$ Å^{-1}. The isotropic thermal parameters, B, are calculated from $B=4[V^2 \det(\beta_{ij})]^{1/3}$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B
C(1)	2·19 (4)	2·22 (4)	1·99 (3)	0·06 (3)	0·20 (3)	-0·10 (3)	2·12
C(2)	1·78 (3)	1·71 (3)	2·09 (3)	-0·03 (3)	0·20 (3)	-0·02 (3)	1·85
C(3)	2·41 (4)	2·46 (4)	2·58 (4)	0·63 (4)	0·21 (3)	0·50 (3)	2·39
C(4)	3·15 (5)	2·67 (4)	2·85 (5)	0·14 (5)	1·03 (4)	0·02 (4)	2·76
C(5)	2·62 (5)	3·03 (5)	2·56 (4)	-0·31 (4)	-0·05 (4)	-0·57 (4)	2·68
C(6)	2·21 (4)	2·07 (4)	3·08 (5)	-0·31 (3)	0·16 (3)	-0·38 (4)	2·38
C(7)	2·34 (4)	2·10 (3)	2·21 (4)	-0·25 (4)	0·16 (3)	0·01 (2)	2·20
N(1)	4·80 (9)	4·34 (8)	5·38 (9)	0·72 (8)	3·06 (8)	0·24 (7)	4·11
N(2)	3·85 (6)	3·71 (6)	4·55 (7)	-1·19 (6)	-0·14 (6)	-0·97 (6)	3·79
N(3)	2·52 (5)	3·29 (5)	5·38 (8)	-0·78 (4)	0·08 (5)	-1·08 (6)	3·38
N(4)	3·79 (6)	3·40 (5)	2·89 (5)	-0·86 (5)	0·71 (5)	0·46 (4)	3·18

Table 3. *Interatomic distances* (Å) *and bond angles* (°)

The estimated standard deviations in parentheses apply to the last digit.

		$(\sin \theta/\lambda_{Mo\,K\alpha}) \geq 0.478$ Å^{-1} data set			
	Uncorrected	Uncorrected	Corrected I*	Corrected II*†	Average
C(1)–C(2)	1·560 (2)	1·559 (2)	1·563		1·563
C(1)–C(3)	1·513 (2)	1·516 (2)	1·519 ⎱		1·518
C(2)–C(3)	1·509 (2)	1·512 (2)	1·517 ⎰		
C(1)–C(4)	1·449 (2)	1·444 (2)	1·447	1·448 ⎫	
C(1)–C(5)	1·451 (2)	1·447 (2)	1·450	1·451 ⎪	1·449
C(2)–C(6)	1·446 (2)	1·443 (2)	1·446	1·447 ⎬	
C(2)–C(7)	1·446 (2)	1·444 (2)	1·447	1·448 ⎭	
C(4)–N(1)	1·137 (2)	1·150 (2)	1·152	1·166 ⎫	
C(5)–N(2)	1·138 (2)	1·149 (3)	1·151	1·159 ⎪	1·160
C(6)–N(3)	1·140 (2)	1·150 (2)	1·152	1·159 ⎬	
C(7)–N(4)	1·138 (2)	1·147 (2)	1·149	1·156 ⎭	
C(3)–H(1)	0·999				
C(3)–H(2)	1·005				

* Corrected for rigid-body thermal motion with parameters determined from the anisotropic thermal parameters of the seven carbon atoms.

† Corrected for riding motion based on ΔU's from the seven carbon atom rigid-body analysis.

Table 3 (cont.)

(sin $\theta/\lambda_{Mo\,K\alpha}$) $\geq$ 0·478 Å^{-1} data set

	Angles*			Angles*
C(1)–C(2)–C(3)	59·1 (1)		C(3)–C(1)–C(4)	118·7 (1)
C(1)–C(3)–C(2)	62·0 (1)		C(3)–C(1)–C(5)	120·1 (1)
C(2)–C(1)–C(3)	58·9 (1)		C(4)–C(1)–C(5)	114·6 (1)
C(1)–C(2)–C(6)	115·8 (1)		C(6)–C(2)–C(7)	116·3 (1)
C(1)–C(2)–C(7)	116·3 (1)		C(1)–C(4)–N(1)	179·2 (4)
C(2)–C(1)–C(4)	116·4 (1)		C(1)–C(5)–N(2)	179·4 (3)
C(2)–C(1)–C(5)	116·7 (1)		C(2)–C(6)–N(3)	177·2 (5)
C(3)–C(2)–C(6)	118·6 (1)		C(2)–C(7)–N(4)	177·1 (4)
C(3)–C(2)–C(7)	118·4 (1)			

* Corrected for rigid-body thermal motion with parameters determined from the anisotropic thermal parameters of the seven carbon atoms.

The cyclopropane ring

In the cyclopropane ring of TCCP the thermally corrected C(1)–C(2) bond length is 1·563 Å; this is considerably longer than the normal value of 1·510 Å found in cyclopropane (Bastiansen, Fritsch & Hedberg, 1964). This result is consistent with the marked weakening that was anticipated for a ring bond adjacent to four strong π-electron acceptors in a substituted cyclopropane. In 2,5-dimethyl-7,7-dicyanonorcaradiene (Fritchie, 1966), the cyclopropane ring bonds adjacent to the two cyano groups are similarly lengthened to a mean value of 1·557 Å. This suggests that additional cyano groups have little incremental effect on the adjacent bonds. Moreover, C–C bond lengths of about 1·56 Å are reported for cyclopropane rings
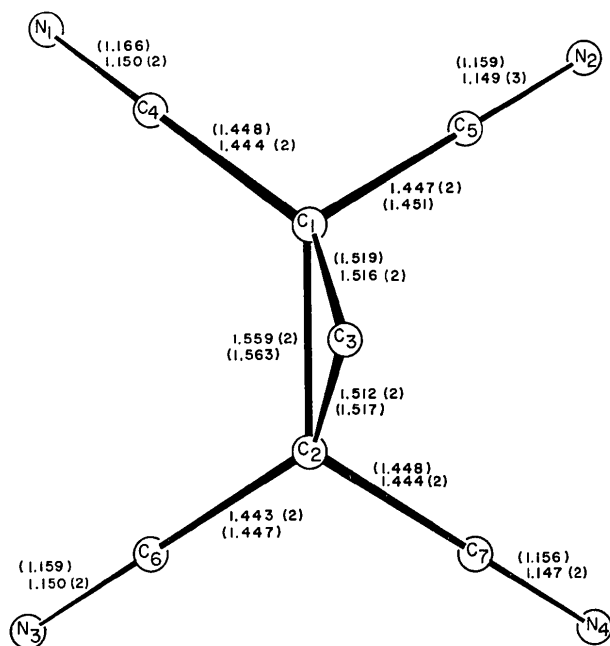

Fig. 2. The 1,1,2,2-tetracyanocyclopropane molecule showing uncorrected bond lengths and standard deviations. Bond lengths corrected for thermal and riding motion appear in parentheses. Both sets of parameters are based on the refinement in which reflections with sin $\theta/\lambda_{Mo\,K\alpha}$ < 0·478 were excluded.

substituted with π-electron acceptors that are weaker than the cyano group (Peterson, 1956; Grant & Speakman, 1958). Thus, we conclude that the easily achieved increase in ring bond length of about 0·05 Å essentially reflects a saturation of the lengthening effect of π-electron withdrawing groups σ-bonded to the cyclopropane ring.

The C(1)–C(3) and C(2)–C(3) bonds in TCCP, in which two vicinal and two distal effects are opposed, have a mean length of 1·518 Å. This value is identical to that observed in cis-1,2,3-tricyanocyclopropane (Hartman & Hirshfeld, 1966) in which vicinal and distal effects are similarly opposed.

The CN groups

Consistent with results for tetracyanoethylene (TCNE) (Little, Pautler & Coppens, 1971) the C≡N bonds, foreshortened in the analysis based on the complete data set, were systematically and uniformly lengthened when lower-angle data were excluded from the refinement. A similar result was recently observed by Hoard (1975) in an analysis of the ring system in porphyrins, wherein there is considerable delocalization of the bonding electrons. It appears that an optimal result is achieved when reflections that are strongly dependent upon the bonding electron distributions are eliminated from the final refinements. As can be seen from the extrapolation of the scattering power of the two core electrons of carbon in Fig. 1, these reflections appear below a value of about 0·5 > sin θ/λ > 0·4.

The average increase in the length of the C≡N bonds in TCCP upon elimination of the low-angle data was 0·011 ± 0·001 Å; all other bond lengths remained essentially unchanged. The C≡N bond lengths before thermal corrections ranged from 1·147 to 1·150 Å with a mean value of 1·149 Å; after correction for thermal motion based on a seven carbon atom rigid-body and a subsequent riding motion correction, the C≡N bonds ranged from 1·156 to 1·166 Å. The mean value, 1·160 Å, is consistent with those obtained by Hanson (1965), 1·160 (7) Å, Greenberg & Post (1968), 1·158 (8) Å, and by Little, Pautler & Coppens (1971), 1·166 (2) Å. It is likewise consistent with C≡N bond lengths obtained by electron diffraction, e.g. 1·162 reported for TCNE (Hope, 1968).

The thermally corrected mean value of 1·449 Å observed for the C(ring)–C(cyano) bonds lies near the center of a range of about 0·04 Å for corresponding bonds in the above-mentioned reports. We observe a slight nonlinearity in the C–C≡N groups that is comparable to that found in many other molecules; this effect has been discussed in detail by Matthews, Swanson, Mueller & Stucky (1971).

Molecular packing

The molecular packing in this crystal structure resembles that described for tetracyanoethylene oxide

(TCEO) (Matthews et al., 1971) in that three of the nitrogen atoms of a molecule, N(2), N(3) and N(4) are closely approached (<3.4 Å) by C(cyano)–C(ring)–C(cyano) groups of another molecule, while the fourth, N(1), is relatively unconfined by intermolecular contacts (Table 4). The isotropic equivalent thermal parameters for the nitrogen atoms (Table 2) clearly increase as the number of such close approaches to carbon atoms decreases. Riding corrections calculated for the $C\equiv N$ bonds follow the same pattern, that for N(1), 0·014 Å, being significantly larger than those for N(2), N(3) and N(4) which are 0·008, 0·007 and 0·007 Å, respectively. It is clear that the riding motion analysis for the least constrained nitrogen atom conforms best to the requirement that the residual motion of the N atom not be correlated with displacements of the C atom; nevertheless, it does not necessarily follow that the corrections to the other three $C\equiv N$ bonds are underestimated. We cannot rule out the possibility that the variation observed in the final corrected $C\equiv N$ bond lengths represents a real variation of about 0·01 Å in equilibrium internuclear distance for $C\equiv N$ bonds in different environments. An intermolecular donor–acceptor interaction as proposed by Matthews et al. (1971) might contribute to such a variation. Clearly, more work is needed in the application of more elaborate thermal analysis techniques (Johnson, 1969) to structures containing several $C\equiv N$ bonds before the matter is resolved.

Table 4. *Selected intermolecular distances involving nitrogen atoms*: $d_{N-H} \leq 3\cdot 0$ Å, $d_{N-C} \leq 3\cdot 4$ Å

All values are derived from data with $(\sin \theta/\lambda_{Mo\,K\alpha}) \geq 0\cdot 478$ Å^{-1}. The nitrogen atoms are in molecule 1, the reference molecule.

	Molecule 2*	Distance (Å)	Mean d_{N-C} (Å)
N(1)–H(1)	655 2_1^y	2·46	
N(2)–H(1)	565	2·88	
N(2)–C(3)	755 2_1^y	3·207 (3)	
N(2)–C(1)	755 2_1^y	3·393 (2)	3·300
N(3)–H(2)	455	2·57	
N(3)–C(7)	455 2_1^x	3·067 (2)	
N(3)–C(2)	455 2_1^x	3·081 (2)	3·096
N(3)–C(6)	455 2_1^x	3·140 (2)	
N(4)–C(6)	565 2_1^x	3·058 (2)	
N(4)–C(2)	565 2_1^x	3·079 (2)	
N(4)–C(1)	565 2_1^x	3·164 (2)	
N(4)–C(7)	565 2_1^x	3·195 (2)	3·172
N(4)–C(4)	565 2_1^x	3·224 (2)	
N(4)–C(5)	565 2_1^x	3·312 (3)	

* The first three digits give lattice translations according to the convention of the Oak Ridge programs (Busing, Martin & Levy, 1964). Translations for the indicated 2_1 axes are positive.

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