Table 7. *Atom parameters of cuprobismutite used to
calculate the intensities listed in Table 6*

	x	y	z	B
Bi(1)	0	0	$\frac{1}{4}$	2·5
Bi(2)	0·256	$\frac{1}{4}$	0·129	2·5
Bi(3)	0·009	0	0·220	2·5
Bi(4)	0·174	$\frac{1}{4}$	0·406	2·5
Cu(1)	0·412	0	0·021	3·5
Cu(2)	0·357	0	0·358	3·5
S(1)	0·337	$\frac{1}{4}$	0·006	1·5
S(2)	0·033	$\frac{1}{4}$	0·110	1·5
S(3)	0·350	0	0·209	1·5
S(4)	0·163	0	0·275	1·5
S(5)	0·017	$\frac{1}{4}$	0·380	1·5
S(6)	0·338	$\frac{1}{4}$	0·440	1·5

octahedral coordination may be less favourable to bismuth than the other types such as trigonal or tetragonal pyramids, it is likely that other elements (*e.g.* Pb, Fe and so forth), even in small amounts, catalyse the formation of these compounds (Moh, 1973). Therefore $Cu_4Bi_5S_{10}$, hodrushite and cuprobismutite may belong to a quarternary system, M–Cu–Bi–S (M: Pb, Fe), with a small amount of M, or they may be formed in the Cu–Bi–S system as a metastable phase only under the condition that a small amount of M is present. A similar behaviour of minor elements has been reported by Bernhardt (1972) in his study on the sulphide system, Cu_2FeSnS_4–$CuFeS_2$.

The authors thank Professor G. Moh (Heidelberg) who supplied the synthetic specimen of cuprobismutite, and Dr E. Makovický (København) for valuable discussions. The computation was performed on the UNIVAC 1108 of the Gesellschaft für Wissensshaftliche Datenverarbeitung, Göttingen.

References

BERNHARDT, H.-J. (1972). *Neues Jb. Miner. Mh.* pp. 553–556.

BERRY, L. G. & THOMPSON, R. M. (1962). *X-ray Powder Data for Ore Minerals: The Peacock Atlas, Geol. Soc. Amer. Mem.* **85**, 281.

BUHLMANN, E. (1971). *Neues Jb. Miner. Mh.* pp. 137–141.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Oak Ridge National Laboratory Report ORNL-TM-305.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., Tables 3.3.1, 3.3.3. Birmingham: Kynoch Press.

KODERA, M., KUPČÍK, V. & MAKOVICKÝ, E. (1970). *Miner. Mag.* **37**, 641–648.

KUPČÍK, V. (1972). In Wedepohl: *Handbook of Geochemistry*, Vol. II/3, 83-A.

KUPČÍK, V. & MAKOVICKÝ, E. (1968). *Neues Jb. Miner. Mh.* pp. 236–237.

LE BIHAN, M.-TH. (1962). *Bull. Soc. Fr. Minér. Crist.* **85**, 15–47.

MOH, G. (1973). Private communication.

NUFFIELD, E. W. (1952). *Amer. Min.* **37**, 447–452.

OHMASA, M. & NOWACKI, W. (1973). *Z. Kristallogr.* **137**, 422–432.

RABENAU, A. & RAU, H. (1969). Private communication.

SUGAKI, A. & SHIMA, H. (1971). *Proceedings of the IMA-IAGOD Meetings*, 1970. IMA Volume, Special Paper No. 1, pp. 270–271.

TAYLOR, C. M., RADTKE, A. S. & CHRIST, C. L. (1973). *J. Res. U.S. Geol. Surv.* **1**, 99–103.

The Structure of 2,3-Dichloro-1,1-dicyano-3,3-diphenylpropene

BY R. SCHLODDER AND JAMES A. IBERS

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, *U.S.A.*

The crystal and molecular structure of 2,3-dichloro-1,1-dicyano-3,3-diphenylpropene, $C_{17}Cl_2H_{10}N_2$, has been determined from 2067 X-ray data above background collected by counter methods. The material crystallizes with eight molecules in space group *Pbca* (D_{2h}^{15}) of the orthorhombic system in a cell of dimensions $a = 15·403$ (3), $b = 19·219$ (4), $c = 10·138$ (2) Å. The observed and calculated densities are 1·39 (1) and 1·386 g cm^{-3}. The structure has been solved by direct methods and refined by full-matrix least-squares methods to a final R index on F of 0·036. The C=C(CN)$_2$ portion of the molecule closely resembles that in tetracyanoethylene. Whereas the olefinic C–Cl bond length is 1·715 (2) Å, the paraffinic C–Cl bond length is 1·836 (2) Å. The material was prepared by the reaction of diphenylcarbene with 1,1-dichloro-2,2-dicyanoethylene. The structure found here indicates that the reaction involves the insertion of diphenylcarbene into a C–Cl bond.

Introduction

In an earlier investigation of the bonding of the unsymmetrical olefin 1,1-dichloro-2,2-dicyanoethylene to a transition metal the complex Pt[Cl$_2$C=C(CN)$_2$][P(C$_6$H$_5$)$_3$]$_2$ was prepared and its structure determined (McAdam, Francis & Ibers, 1970). Because of the difference in Pt–C (of Cl) *versus* Pt–C (of CN) bond

lengths, 2·00 (2) vs. 2·10 (2) Å, it was our desire to compare this structure with that of an analogous cyclopropane in which the metal center had been replaced by a CR_2 group. Toward that end considerable effort was expended in the attempted synthesis of 1,1-dichloro-2,2-dicyano-3,3-diphenylcyclopropane. A compound having the correct analysis was finally obtained. In the absence of ^{13}C n.m.r. data there was no spectroscopic means, including mass spectra, which would enable us unambiguously to determine whether we had prepared the desired product or the isomer 2,3-dichloro-1,1-dicyano-3,3-diphenylpropene. The propene was a possibility from the preparative route. On the basis of the structure determination reported here the desired product was not obtained but rather the compound prepared is the propene.

Experimental

The attempted synthetic route of choice was the reaction of diphenylcarbene with 1,1-dichloro-2,2-dicyanoethylene. Diphenyldiazomethane (1·94 g, 0·01 mole) was added in small portions to a solution of 1·47 g (0·01 mole) of 1,1-dichloro-2,2-dicyanoethylene in 20 ml of ether. The deep-red solution was allowed to stand for four days at room temperature. After partial removal of the solvent and cooling, a slightly yellow solid could be isolated. On the basis of its melting point and infrared spectrum this compound was identified as tetraphenylethylene. The remaining solution was kept at room temperature for two more days, the solvent was then partially removed, and the solution was put into a refrigerator for 12 h. Colorless crystals were thus obtained. The crystals were recrystallized from ether. M.p. 137–138°C, infrared spectrum (in KBr) 3074 (m) (ν C–H), 2237 (m) (ν C≡N), 1559 (m) (ν C=C) cm^{-1}. Analysis calculated for $C_{17}H_{10}N_2Cl_2$: C, 65·20; H, 3·22; N, 8·95%; found C, 64·82; H, 3·17; N, 8·34%. The mass spectrum shows the masses $m/e = 277^+$ and 279^+ ($C_{17}H_{10}ClN_2$) and 242^+ ($C_{17}H_{10}N_2$). The parent peak could not be detected.

A similar procedure, using diazomethane in place of diphenyldiazomethane, yields a product whose elemental analyses, infrared spectrum, and ^1H-n.m.r. spectrum are suggestive of insertion of a carbene into each C–Cl bond of the olefin 1,1-dichloro-2,2-dicyanoethylene and addition of a third carbene to form 1,1-dicyano-2,2-bis(chloromethylene)cyclopropane. M. p. 139–140°C; infrared spectrum (in KBr) 3102 (m), 3019 (m), 2974 (m) (ν C–H), 2265 (sh), 2254 (s) (ν C≡N) cm^{-1}; n.m.r. (in D_3CCOCD_3), two peaks at δ 3·57 and 2·07 (ratio 2:1); analysis calculated for $C_7H_6Cl_2N_2$: C, 44·48; H, 3·20; N, 14·82%; found: C, 44·31; H, 3·61; N, 14·49%.

On the basis of precession and Weissenberg photography taken with Cu $K\alpha$ radiation, the crystals were assigned to space group $Pbca$ (D_{2h}^{15}) of the orthorhombic system (systematic absences: $0kl$, k odd; $h0l$, l odd; $hk0$, h odd). Lattice parameters were obtained from a least-squares analysis of the setting angles of 13 reflections in the 2θ range 25 to 30° which had been centered on a FACS-I diffractometer using a takeoff angle of 1·5° and Mo $K\alpha_1$ radiation ($\lambda = 0·70930$ Å) monochromatized from the (002) face of a highly mosaic graphite crystal (Doedens & Ibers, 1967). Crystal data are in Table 1.

Table 1. *Crystal data*

$C_{17}Cl_2H_{10}N_2$ F.W. 313·19
Space group $Pbca$ (D_{2h}) $Z=8$
$a = 15·403$ (3), $b = 19·219$ (4), $c = 10·138$ (2) Å, $V = 3000$ Å^3
$D_o = 1·39$ (1) (by flotation), $D_c = 1·386$ g cm^{-3}, $\mu = 4·25$ cm^{-1}

Intensity data were collected on a FACS-I diffractometer from a parallelepiped-shaped crystal of approximate dimensions 0·5 mm long ([100] direction) and of approximate cross-section 0·4 mm (girdle faces {021}), calculated volume 0·062 mm³. The crystal was mounted with the [100] direction offset from the spindle direction by about 4°. Data collection methods have been detailed previously (Doedens & Ibers, 1967; Corfield, Doedens & Ibers, 1967). Data were collected
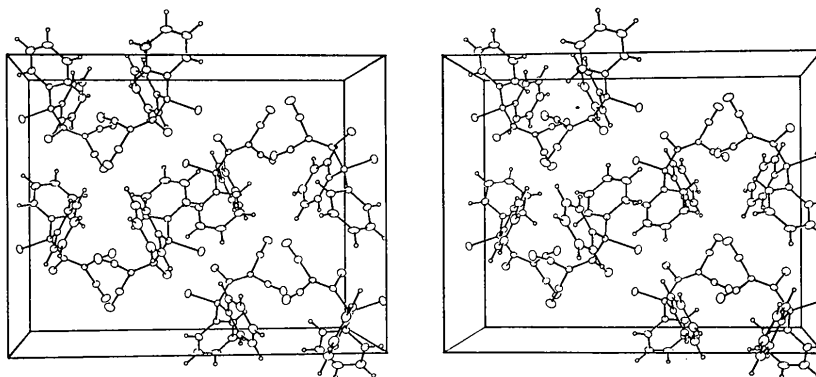

Fig. 1. A stereo view of the unit cell of 2,3-dichloro-1,1-dicyano-3,3-diphenylpropene. The 20% probability ellipsoids are shown, except for the hydrogen atoms which have been drawn artificially small. The view is down z, with x running from left to right and y from bottom to top.

out to 2θ (Mo) of $52°$. Past this point there were few data significantly above background. Background counts were taken for 10 s at each end of the scan range for $2\theta < 30°$, and for 20 s thereafter. The scan rate was $2°$ in 2θ min^{-1} from $0.9°$ below the $K\alpha_1$ peak to $1.0°$ above the $K\alpha_2$ peak. The counter was 32 cm from the crystal and was preceded by an aperture 3 mm wide by 5.5 mm high. The takeoff angle was $1.8°$.

3365 reflections were scanned. These scans yielded 2067 unique reflections which obeyed the condition $F_o^2 > 3\sigma(F_o^2)$, where a value of p of 0.03 was used in the calculation of $\sigma(F_o^2)$. These reflections were used in subsequent calculations. Six standard reflections, meas-

ured at intervals of 100, were constant within counting statistics.

The structure was solved by symbolic addition using 308 rescaled values of $E > 1.76$. The course of the refinement is detailed in Table 2.

Tests for the effects of absorption led to minimum and maximum transmission factors of 0.85 and 0.89, respectively, and so no correction for absorption was made. An inspection of $|F_o|$ vs. $|F_c|$ did not suggest the need for an extinction correction. Atomic scattering factors were taken from Cromer & Waber (1974); the

Table 2. *Course of the refinement*

Model	R^*	R_w^*
Phenyl atoms as groups; all other non-hydrogen atoms isotropic, H atoms ignored	0·121	0·156
Nongroup atoms anisotropic	0·085	0·110
H atoms added [C–H = 0·95 Å, B(H) = equivalent B of C + 1·0 Å^2] as fixed contributions	0·061	0·075
All nonhydrogen atoms anisotropic; H atoms as above	0·036	0·044

Error in observation of unit weight	1·71 e (190 variables, 2067 observations)
Maximum electron density on final difference Fourier map	0·15 (3) e Å^{-3}
Number of unobserved reflections having $|F_o^2 - F_c^2| < 3\sigma(F_o^2)$	None
Trends of $\sum w(|F_o| - |F_c|)^2$ with setting angles, $|F_o|$, Miller indices	None

* $R = \sum ||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ where $w = 4F_o^2/\sigma^2(F_o^2)$ and refinement is on F.
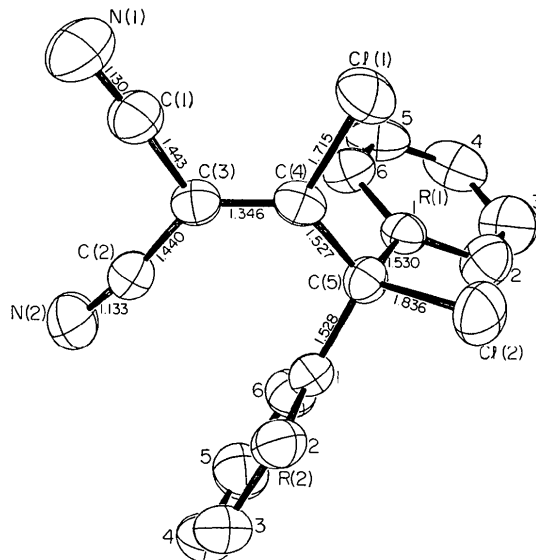

Fig. 2. A drawing of the 2,3-dichloro-1,1-dicyano-3,3-diphenyl-propene molecule with hydrogen atoms omitted. The 50 % probability ellipsoids are shown.

Table 3. *Final parameters for 2,3-dichloro-1,1-dicyano-3,3-diphenylpropene*

The form of the anisotropic thermal ellipsoid is exp$[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Here and in succeeding tables estimated standard deviations are parenthesized.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	0·75154 (5)	0·57812 (4)	0·62096 (7)	0·00512 (3)	0·00326 (2)	0·01140 (8)	0·00030 (2)	0·00229 (4)	−0·00158 (3)
Cl(2)	0·66310 (5)	0·48798 (3)	0·83624 (7)	0·00582 (4)	0·00207 (2)	0·01271 (8)	0·00059 (2)	−0·00092 (4)	0·00041 (3)
N(1)	0·8603 (2)	0·7404 (1)	0·6732 (3)	0·0051 (1)	0·0047 (1)	0·0157 (3)	−0·0013 (1)	0·0021 (2)	0·0006 (2)
N(2)	0·6789 (2)	0·7652 (1)	0·9654 (2)	0·0073 (1)	0·0028 (1)	0·0129 (3)	−0·0005 (1)	0·0020 (2)	−0·0015 (1)
C(1)	0·8044 (2)	0·7119 (1)	0·7211 (3)	0·0037 (1)	0·0030 (1)	0·0097 (3)	−0·0003 (1)	0·0004 (2)	−0·0001 (1)
C(2)	0·6984 (2)	0·7238 (1)	0·8915 (2)	0·0038 (1)	0·0023 (1)	0·0091 (3)	−0·0004 (1)	0·0003 (1)	0·0001 (1)
C(3)	0·7326 (1)	0·6797 (1)	0·7892 (2)	0·0028 (1)	0·0023 (1)	0·0076 (2)	0·0000 (1)	0·0002 (1)	0·0001 (1)
C(4)	0·7023 (1)	0·6167 (1)	0·7538 (2)	0·0028 (1)	0·0025 (1)	0·0068 (2)	0·0005 (1)	0·0001 (1)	−0·0002 (1)
C(5)	0·6250 (1)	0·5776 (1)	0·8123 (2)	0·0034 (1)	0·0018 (1)	0·0082 (2)	0·0002 (1)	0·0000 (1)	0·0002 (1)
R(1)C(1)	0·5499 (2)	0·5774 (1)	0·7134 (2)	0·0032 (1)	0·0024 (1)	0·0071 (2)	−0·0001 (1)	0·0003 (1)	−0·0002 (1)
R(1)C(2)	0·4901 (2)	0·5238 (1)	0·7111 (3)	0·0041 (1)	0·0032 (1)	0·0130 (3)	−0·0008 (1)	−0·0005 (2)	0·0004 (1)
R(1)C(3)	0·4209 (2)	0·5263 (2)	0·6252 (3)	0·0045 (1)	0·0049 (1)	0·0160 (4)	−0·0011 (1)	−0·0015 (2)	−0·0005 (2)
R(1)C(4)	0·4104 (2)	0·5818 (2)	0·5421 (3)	0·0035 (1)	0·0062 (1)	0·0112 (3)	0·0003 (1)	−0·0012 (2)	−0·0015 (2)
R(1)C(5)	0·4681 (2)	0·6363 (2)	0·5454 (3)	0·0041 (1)	0·0051 (1)	0·0089 (3)	0·0009 (1)	−0·0002 (2)	0·0010 (2)
R(1)C(6)	0·5383 (2)	0·6342 (1)	0·6313 (2)	0·0037 (1)	0·0032 (1)	0·0094 (3)	−0·0001 (1)	−0·0004 (1)	0·0008 (1)
R(2)C(1)	0·5993 (1)	0·6050 (1)	0·9483 (2)	0·0035 (1)	0·0021 (1)	0·0075 (2)	−0·0003 (1)	0·0005 (1)	0·0003 (1)
R(2)C(2)	0·6564 (2)	0·5991 (1)	1·0538 (2)	0·0046 (1)	0·0029 (1)	0·0084 (3)	−0·0003 (1)	−0·0002 (2)	0·0008 (1)
R(2)C(3)	0·6353 (2)	0·6279 (2)	1·1744 (3)	0·0067 (2)	0·0036 (1)	0·0078 (3)	−0·0008 (1)	−0·0001 (2)	0·0007 (1)
R(2)C(4)	0·5579 (2)	0·6619 (2)	1·1920 (3)	0·0075 (2)	0·0040 (1)	0·0087 (3)	−0·0009 (1)	0·0024 (2)	−0·0006 (1)
R(2)C(5)	0·4996 (2)	0·6656 (2)	1·0895 (3)	0·0051 (1)	0·0040 (1)	0·0128 (4)	−0·0001 (1)	0·0027 (2)	−0·0012 (2)
R(2)C(6)	0·5201 (2)	0·6377 (1)	0·9667 (2)	0·0039 (1)	0·0031 (1)	0·0100 (3)	0·0000 (1)	0·0009 (2)	−0·0003 (1)

values of $\Delta f'$ and $\Delta f''$ were taken from Cromer (1974); these were included in the calculation of F_c (Ibers & Hamilton, 1964).*

Table 3 lists the values of the atomic parameters while Table 4 lists the calculated positions of the H atoms.

Table 4. Calculated parameters for H atoms

	x	y	z	$B(\text{Å}^2)$
R(1)H(2)*	0·498	0·484	0·768	5·7
R(1)H(3)	0·380	0·488	0·623	6·9
R(1)H(4)	0·362	0·584	0·483	6·5
R(1)H(5)	0·461	0·676	0·488	6·0
R(1)H(6)	0·579	0·672	0·633	5·0
R(2)H(2)	0·711	0·576	1·041	5·0
R(2)H(3)	0·676	0·624	1·246	5·9
R(2)H(4)	0·543	0·681	1·276	6·4
R(2)H(5)	0·445	0·689	1·101	6·3
R(2)H(6)	0·480	0·642	0·895	5·1

* R(1)H(2) is attached to R(1)C(2), *etc.*

Description of the structure

The structure consists of well separated molecules of the propene. The distance of closest approach is 2·33 Å between R(2)H(2) and R(1)H(4) on adjacent molecules. A stereo view of the unit cell is presented in Fig. 1. A drawing of the molecule, including the labeling scheme and principal distances, is shown in Fig. 2. Table 5 presents selected distances and angles, together

* A list of structure amplitudes ($10|F_o|$ and $10|F_c|$ for 2067 reflections) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30727 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

with their standard deviations as estimated from the inverse matrix.

Best weighted least-squares planes through the two phenyl rings and through the propene molecule are presented in Table 6. The deviations from planarity

Table 6. Best weighted least-squares planes

Plane equation: $Ax + By + Cz = D$, with x,y,z in crystal coordinates.

Plane	A	B	C	D
1	8·432	−8·778	−7·108	−5·510
2	6·434	16·647	−2·770	11·289
3	9·682	−8·486	6·490	6·410

Deviations from planes (Å)

	1	2	3
Cl(1)			−0·0092 (8)
Cl(2)			1·296
N(1)			0·005 (3)
N(2)			−0·065 (3)
C(1)			0·017 (3)
C(2)			−0·004 (3)
C(3)			0·038 (2)
C(4)			0·048 (2)
C(5)	−0·0641	0·0980	0·011 (2)
R(1)C(1)	0·008 (2)*		−1·356
R(1)C(2)	−0·009 (3)		
R(1)C(3)	−0·005 (3)		
R(1)C(4)	0·010 (3)		
R(1)C(5)	−0·005 (3)		
R(1)C(6)	−0·006 (3)		
R(2)C(1)		0·011 (2)	0·414
R(2)C(2)		−0·012 (2)	
R(2)C(3)		−0·002 (3)	
R(2)C(4)		0·018 (3)	
R(2)C(5)		−0·012 (3)	
R(2)C(6)		−0·005 (3)	

* Estimated standard deviations are given only for those atoms used in the calculation of a given plane.

Table 5. Selected distances (Å) and angles (°) in 2,3-dichloro-1,1-dicyano-3,3-diphenylpropene

Cl(1)——C(4)	1·715 (2)		N(1)——C(1)——C(3)	175·7 (3)
Cl(2)——C(5)	1·836 (2)		N(2)——C(2)——C(3)	170·5 (3)
N(1)——C(1)	1·130 (3)		C(1)——C(3)——C(2)	112·0 (2)
N(2)——C(2)	1·133 (3)		C(1)——C(3)——C(4)	121·6 (2)
C(3)——C(1)	1·443 (3)		C(2)——C(3)——C(4)	126·4 (2)
C(3)——C(2)	1·440 (3)		C(3)——C(4)——Cl(1)	116·4 (2)
C(3)——C(4)	1·346 (3)		C(3)——C(4)——C(5)	127·5 (2)
C(4)——C(5)	1·527 (3)		Cl(1)——C(4)——C(5)	115·9 (2)
C(5)——R(1)C(1)	1·530 (3)		C(4)——C(5)——R(1)C(1)	109·6 (2)
C(5)——R(2)C(1)	1·528 (3)		C(4)——C(5)——R(2)C(1)	112·5 (2)
R(1)C(1)–R(1)C(2)	1·382 (3)		C(4)——C(5)——Cl(2)	105·2 (1)
R(1)C(2)–R(1)C(3)	1·377 (4)		R(1)C(1)–C(5)——R(2)C(1)	113·4 (2)
R(1)C(3)–R(1)C(4)	1·369 (4)		R(1)C(1)–C(5)——Cl(2)	109·0 (1)
R(1)C(4)–R(1)C(5)	1·375 (4)		R(2)C(1)–C(5)——Cl(2)	106·6 (1)
R(1)C(5)–R(1)C(6)	1·388 (4)		R(1)C(1)–R(1)C(2)–R(1)C(3)	120·0 (3)
R(1)C(6)–R(1)C(1)	1·384 (3)		R(1)C(2)–R(1)C(3)–R(1)C(4)	120·6 (3)
R(2)C(1)–R(2)C(2)	1·389 (3)		R(1)C(3)–R(1)C(4)–R(1)C(5)	120·1 (3)
R(2)C(2)–R(2)C(3)	1·381 (4)		R(1)C(4)–R(1)C(5)–R(1)C(6)	119·8 (3)
R(2)C(3)–R(2)C(4)	1·370 (4)		R(1)C(5)–R(1)C(6)–R(1)C(1)	120·1 (2)
R(2)C(4)–R(2)C(5)	1·375 (4)		R(1)C(6)–R(1)C(1)–R(1)C(2)	119·5 (2)
R(2)C(5)–R(2)C(6)	1·392 (4)		R(2)C(1)–R(2)C(2)–R(2)C(3)	120·0 (2)
R(2)C(6)–R(2)C(1)	1·386 (3)		R(2)C(2)–R(2)C(3)–R(2)C(4)	120·7 (3)
			R(2)C(3)–R(2)C(4)–R(2)C(5)	119·6 (3)
			R(2)C(4)–R(2)C(5)–R(2)C(6)	120·6 (3)
			R(2)C(5)–R(2)C(6)–R(2)C(1)	119·6 (2)
			R(2)C(6)–R(2)C(1)–R(2)C(2)	119·4 (2)

are small in each instance. The planes are nearly perpendicular to each other, the dihedral angles between the planes being 88·6 (1,2), 84·4 (1,3), and 107·2° (2,3).

The phenyl rings have their expected geometry. The average C–C distance in the two rings is 1·382 Å. The standard deviation of a single observation, as estimated from the averaging of the 12 values, is 0·008 Å. That this estimate of the standard deviation is about twice that estimated from the inverse matrix is probably the result of the effects of thermal motion on the apparent distances in the rings. In each instance the shortest distances are associated with C(4) at the periphery of the ring. The bond angles within the rings average 120·00° with an estimated standard deviation of a single observation of 0·45°.

The bond distances in the C=C(CN)$_2$ portion of the molecule are in excellent agreement with those of Little, Pautler & Coppens (1971) for tetracyanoethylene. Thus values for the present structure and for cubic tetracyanoethylene are: C=C, 1·346 (3), 1·344 (3); C–C, 1·440 (3) and 1·443 (3), 1·437 (2); C–N, 1·130 (3) and 1·133 (3), 1·135 (2) Å. The bond angles, which are more sensitive to packing forces, differ somewhat: C–C–N, 170·5 (3) and 175·7 (3), 178·2 (1); C–C–C(exo), 112·0 (2), 115·6 (1); C–C–C(endo), 121·6 (2) and 126·4 (2), 122·2 (1)°.

The C(4)–C(5) bond length of 1·527 (3) Å is somewhat longer than the equivalent bond of 1·488 Å in propene (Lide & Mann, 1957), but there appear to be no 3-chloropropene structures for direct comparison.

The most interesting feature of the present structure is the comparison of the C(olefinic)–Cl distance of 1·715 (2) Å with the C(paraffinic)–Cl distance of 1·836 (2) Å. There appear to be no other structures where this direct comparison can be made. The shorter C–Cl distance is in excellent agreement with that of 1·719 (5) Å given by Sutton (1965) for the average olefinic C–Cl bond in 12 complexes. Comparable C–Cl bonds [1·715 (11) and 1·701 (12) Å] were observed in 1,2,3,4-tetrachlorobutadiene (Otaka, 1972). On the other hand, the paraffinic C–Cl bond length of 1·836 (2) Å observed in the present structure is longer than the value of 1·78–1·79 Å expected for a normal paraffinic C–Cl bond (Altona, Knobler & Romers, 1963). Some bonds of roughly comparable length are 1·800 (6) and 1·814 (5) Å in the cage compound C$_{16}$H$_{14}$OCl$_2$ (Shimanouchi & Sasada, 1970), 1·837 (7) and 1·809 (9) Å in 2,3-bis-(cis-4-chloro-l-methylcyclohexyl)-trans-2-butene (Mootz, 1968), and 1·839 (13) Å in α-cyclotropane monohydrate (Vooren, Schenk & MacGillavry, 1970). In general, long C–Cl bonds are observed in compounds containing a highly reactive C–Cl bond. For example, in allyl chloride the C–Cl bond length is 1·82 Å (Bowen, Gilchrist & Sutton, 1955), in acetyl chloride it is 1·82 Å (Allen & Sutton,

1951), in trans-2,5-dichloro-1,4-dioxane it is 1·845 (6) Å (Altona, Knobler & Romers, 1963), and in 2β,3α-dichloro-5α-cholestane C–Cl bond lengths of 1·80 and 1·82 Å are found (Geise, Romers & Rutten, 1966). The fact that the molecular peak is not observable in the mass spectrum of the present compound is indicative of a reactive C–Cl bond.

Computer programs used in this work include, in addition to local programs for the CDC 6400, local modifications of Zalkin's FORDAP Fourier summation program, the Busing–Levy ORFLS error program, Dewar's FAME program for the calculation of E's, and the Main–Woolfson–Germain LSAM symbolic addition program. Our least-squares program, NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.

References

ALLEN, P. W. & SUTTON, L. E. (1951). Trans. Faraday Soc. 47, 236.

ALTONA, C., KNOBLER, C. & ROMERS, C. (1963). Acta Cryst. 16, 1217.

BOWEN, H. J. M., GILCHRIST, A. & SUTTON, L. E. (1955). Trans. Faraday Soc. 51, 1341.

CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). Inorg. Chem. 6, 197–204.

CROMER, D. T. (1974). International Tables for X-ray Crystallography, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press.

CROMER, D. T. & WABER, J. T. (1974). International Tables for X-ray Crystallography, Vol. IV, Table 2.2A. Birmingham: Kynoch Press.

DOEDENS, R. J. & IBERS, J. A. (1967). Inorg. Chem. 6, 204–210.

GEISE, H. J., ROMERS, C. & RUTTEN, E. W. M. (1966). Acta Cryst. 20, 249–257.

IBERS, J. A. & HAMILTON, W. C. (1964). Acta Cryst. 17, 781–782.

LIDE, D. R. JR & MANN, D. E. (1957). J. Chem. Phys. 27, 868–873.

LITTLE, R. G., PAUTLER, D. & COPPENS, C. (1971). Acta Cryst. B27, 1493–1499.

McADAM, A., FRANCIS, J. N. & IBERS, J. A. (1971). J. Organometal. Chem. 29, 149–161.

MOOTZ, D. (1968). Acta Cryst. B24, 839–844.

OTAKA, Y. (1972). Acta Cryst. B28, 342–345.

SHIMANOUCHI, H. & SASADA, Y. (1970). Acta Cryst. B26, 563–577.

SUTTON, L. E. (1965). Tables of Interatomic Distances and Configuration in Molecules and Ions, S17s. London: The Chemical Society.

VOOREN, M., SCHENK, H. & MACGILLAVRY, C. H. (1970). Acta Cryst. B26, 1483–1487.