in an nmr tube. The paramagnetic shifts undergone by various protons (TMS as internal standard) are shown in Table III.

TABLE III

3,5-*exo*,*exo*-Dibenzoate (**2**)	3,5-*endo*,*endo*-Dibenzoate (**3**)	
Hydrogens	Ppm	Ppm
H_1		0
H_2, H_6	0.05	0.12
H_{7c}, H_{7d}	0.07	0
H_4	0.10	0.17
H_3, H_5	0.10	0.27

The chemical shifts and coupling constants obtained in this study were reliable enough to be used for computer simulation of the actual high-field spectra of compounds **3** and **4**. Long-range coupling could not be demonstrated on the simulated spectrum owing to the five-spin computer limitation. However, irradiation of H_4 eliminated the long-range coupling of H_4, resulting in a better correlation of simulated with experimental spectra.

Registry No.—**2**, 4054-86-8; **3**, 4118-49-4; **4**, 17290-03-8; **5**, 24694-55-1.

Acknowledgment.—We are indebted to Mr. C. A. Boye of Tennessee Eastman for furnishing us the basic five-spin computer program and to Dr. E. I. Snyder, Visiting Professor of Chemistry, 1969–1970, for rewriting certain segments of this program to fit the (8K) IBM-1130 at East Tennessee State University. We would also like to acknowledge the aid of Mr. Ogawa at JEOLCO for running the 100-MHz spectra. We acknowledge considerable assistance from the East Tennessee State University Research Advisory Council.

Structure of 1,3-Dicyanobicyclo[1.1.0]butane Using X-Ray Analysis

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Bicyclo[1.1.0]butane and its derivatives are of current interest because of the favorable properties of some of the polymers formed. The structure of bicyclobutane has been assessed using a wide variety of physical methods, including infrared and Raman spectroscopy,[1] microwave spectroscopy,[2,3] electron diffraction,[4] and nuclear magnetic resonance spectroscopy.[5,6] The instability of bicyclobutane makes X-ray diffraction analysis on this compound difficult. However, a substituted bicyclobutane, 1,3-dicyanobicyclobutane (I), is a solid at room temperature and is stable for a sufficient time to collect X-ray data. We wish to report the results of a single-crystal X-ray determination of this substituted bicyclobutane which was kindly supplied to us by Dr. S. C. Cherkofsky of the Du Pont Company.

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Experimental Section

Compound I crystallizes as colorless needles elongated about the *b* crystallographic axis. The lattice constants, as determined by a least-squares analysis on the settings for the angles on a four-angle diffractometer for six reflections (Cu K_α, λ = 1.54178 Å) are a = 10.397 (7), b = 5.813 (4), c = 9.358 (8), V = 566 (2) Å^3. The systematic absences, $0kl$ when $k = 2n + 1$, $h0l$ when $l = 2n + 1$, $hk0$ when $h + k = 2n + 1$, $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, and $00l$ when $l = 2n + 1$, determine the space group to be *Pbcn*. The molecular weight, $C_6N_2H_4$, is 104; $F(000)$ is 216. The observed and calculated densities are 1.20 and 1.22 g cm^{-3}, respectively.

All data in the 2θ range 0–120° were collected with a Picker FACS-I diffractometer. A θ–2θ scan was used; the scan rate was 2 deg/min and 10-sec backgrounds were collected before and after each scan. There were 425 unique reflections of which 321 were considered to be above backround using the criteria $I > 3\sigma(I)$. Lorentz and polarization factors were applied but no absorption corrections were made. The maximum and minimum transmission factors to be applied to the intensities are estimated to be 0.97 and 0.94. A standard reflection was measured every 50th reflection. The intensity of the standard at the end of data collection was 81% of the original. This was corrected for by assuming that the decline in intensity for all reflections followed the decline of the standard. A linear interpolation between each pair of standards was used to arrive at the individual reflections scale factor.

The structure was solved using Long's program for the reiterative application of Sayre's equation.[7] The first E map yielded the positions of all nonhydrogen atoms. After full matrix least-squares refinement, the hydrogen atoms were located from a difference map. Further refinement with carbon and nitrogen vibrating anisotropically while hydrogen vibrated isotropically yielded a final R value of 0.057. The final atomic coordinates are given in Table I and the thermal parameters are in Table II.

TABLE I

FINAL ATOMIC COORDINATES OF DINITRILE BICYCLOBUTANE IN FRACTIONS OF THE UNIT CELL EDGE, WITH STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
N-1	0.3506 (3)	0.5118 (6)	0.0813 (4)
C-2	0.3940 (3)	0.3523 (6)	0.1321 (4)
C-3	0.4492 (3)	0.1507 (5)	0.1929 (3)
C-4	0.4218 (4)	0.0515 (6)	0.3355 (4)
H-5	0.417 (3)	−0.124 (7)	0.340 (4)
H-6	0.367 (3)	0.130 (6)	0.406 (3)

TABLE II

FINAL ANISOTROPIC THERMAL PARAMETERS FOR THE NONHYDROGEN ATOMS EXPRESSED AS exp $-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$. FINAL ISOTROPIC TEMPERATURE FACTORS FOR THE HYDROGEN ATOMS (B_θ Å^2)

	b_{11}(× 10^4)	b_{22}(× 10^4)	b_{33}(× 10^4)	b_{12}(× 10^4)	b_{13}(× 10^4)	b_{23}(× 10^4)
N-1	160 (4)	485 (13)	291 (7)	48 (7)	8 (4)	132 (7)
C-2	121 (4)	396 (13)	171 (5)	−10 (6)	3 (3)	31 (7)
C-3	123 (4)	293 (10)	133 (4)	−6 (5)	−14 (3)	0 (5)
C-4	154 (5)	360 (13)	146 (5)	−47 (6)	5 (4)	18 (7)

	B_θ	
H-5	7.3	(9)
H-6	5.0	(7)

Results and Discussion

The bond lengths are given in Figure 1 and the bond angles are given in Table III. Most of the parameters found in this study are in agreement with the results of previous structural studies using other methods.[1–6] A notable difference comes in the dihedral angle formed

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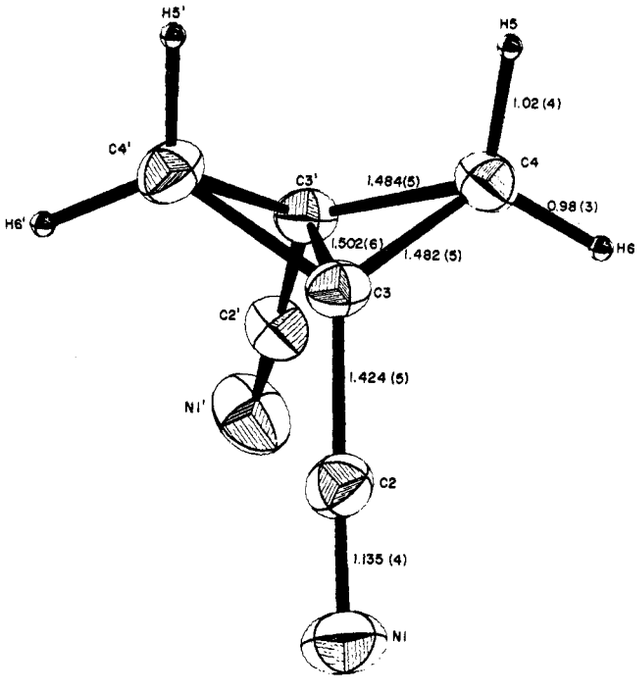

Figure 1.—Bond lengths for 1,3-dicyanobicyclo[1.1.0]butane in angstroms.

TABLE III
INTRAMOLECULAR ANGLES BETWEEN ATOMS OF 1,3-DICYANOBICYCLO[1.1.0]BUTANE

N-1-C-2-C-3	178.8 (3)
C-2-C-3-C-4	127.1 (3)
C-2-C-3-C-3′	124.6 (3)
C-2-C-3-C-4′	127.8 (3)
C-3-C-4-H-5	115.9 (14)
C-3-C-4-H-6	112.3 (12)
C-3-C-4-C-3′	60.9 (2)
C-4-C-3-C-3′	59.6 (2)
C-3-C-3′-C-4	59.5 (2)
C-4-C-3-C-4′	100.6 (3)
C-3-C-4′-H-5′	116.4 (14)
C-3-C-4′-H-6′	117.7 (12)
H-5-C-4-H-6	113.7 (15)

by the two three-membered carbon rings. The X-ray diffraction results of 126.4 ± 0.4° is larger than the values previously found, which ranged from 120.2° to 126°.[1-6] Perhaps the substitution of a nitrile group for hydrogen affects this dihedral angle.

In a survey of previous information on the structure of bicyclobutane, the largest discrepancy occurs in the C–C–H angle corresponding to C_3'–C_3–C_2 of dinitrile bicyclobutane where C_2 is substituted for H. The C–C–C angle found in this paper is 124.6 ± 0.2°, which is in moderate agreement with the microwave spectra[2,3] result of 130° 22′, the nmr spectra[5,6] result of 128.0°, and the electron diffraction result[4] of 125.5°. In contrast, the infrared work[1] placed this angle (CCH) as 163 ± 3°. They do state that the moments of inertia are rather insensitive to this angle.

There are no anomalous intermolecular contacts in this structure. Two interesting intramolecular contacts are the H_5–H_5' distance of 2.42 (5) Å and the C_2–C_2' distance of 3.118 (5) Å. The hydrogen atom repulsions appear to be of little importance because twice the van der Waals radius of hydrogen is about 2.4 Å. However, the C_2–C_2' repulsions may affect the geometry of the bicyclobutane moiety of this compound.

Two review articles on bicyclobutane describe the chemistry of these compounds in detail.[8,9] A model for the electronic structure has been proposed,[10] but, at the time of these calculations, only an inexact knowledge of the structure of bicyclobutane was known. More recently, calculations of the valence electron density distribution[11] and the first excited state charge density[12] have been made for bicyclobutane.

Registry No.—1,3-Dicyanobicyclo[1.1.0]butane, 27184-67-4.

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Buffered Permanganate Reactions. Effect of Calcium on the Rate of Disproportionation of Manganate(VI)

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The pronounced influence pH exerts on the kinetic course of many permanganate oxidations is well recognized.[1] This effect is rarely related to variations in oxidation potential, but can be usually explained by mechanistic factors, such as ionization of the substrate or protonation of permanganate, for example. Furthermore, permanganate oxidations tend to give rise to simultaneous operation of several mechanisms and, consequently, to the formation of multiple reaction products under unfavorable reaction conditions.

Control of pH by employment of suitable buffer systems is a common method for manipulation of yields and product ratios in the application of oxidations to organic synthesis. A typical example is the neutral oxidation of certain organic substrates in Mg^{2+}-ion buffered systems, in which the equilibrium concentration of OH^- ions in solution is limited by the solubility of magnesium hydroxide.[2]

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2\ (s) \qquad (1)$$

Permanganate oxidations of organic compounds often proceed at faster rates in alkaline than in neutral solutions. In many such instances the observed rate enhancement is associated with an increasing degree of substrate ionization. The reaction pattern of alkaline permanganate oxidations is, however, usually highly complex in view of the different pathways by

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