

The Crystal and Molecular Structure of 3,7-Dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane

L. M. Trefonas and J. N. Brown

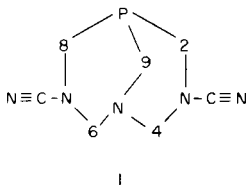
Department of Chemistry, Louisiana State University in New Orleans,
New Orleans, Louisiana 70122

Received September 1, 1972

The crystal and molecular structure of the title compound has been determined by a single crystal x-ray diffraction study using counter-data. The compound crystallizes in the monoclinic space group, $P2_1/c$, with $a = 8.657 \pm .001 \text{ \AA}$, $b = 10.513 \pm .001 \text{ \AA}$, $c = 10.378 \pm .001 \text{ \AA}$, $\beta = 99.68 \pm .01^\circ$ for $Z = 4$. The structure was solved by the symbolic addition procedure and refined by block-diagonal least-squares to $R = 0.052$ for 1479 statistically significant reflections. The geometry of the bicyclic ring system is discussed.

Introduction.

Tris(hydroxymethyl)phosphine (THP) and THP-formaldehyde solutions react with secondary amines given well-defined monomeric products whereas with primary amines, the products are normally polymeric (1,2). While working with solutions containing formaldehyde, THP, cyanamide and phosphoric acid, a white crystalline compound precipitated from solution (3); 3,7-dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane (1).



Since the compound is a polycyclic extension of the systems containing phosphorus and nitrogen as heteroatoms which are currently under investigation in this laboratory (4), an x-ray structure determination was done. In addition to obtaining the physical parameters of interest to us, the structure determination confirmed the previous evidence (3) regarding the identity of the compound.

EXPERIMENTAL

A sample of the title compound was kindly provided by F. L. Normand of the Southern Regional Research Laboratory, New Orleans, Louisiana. It was recrystallized using ethyl-ether and acetonitrile as a solvent-pair, and suitable cylindrical crystals of maximum dimension less than 0.2 mm were selected. The symmetry of the crystal and the cell dimensions were then

determined on a General Electric XRD-5 diffractometer using $\text{Cu-K}\alpha$ radiation. Plots of the reciprocal lattice revealed $2/m$ symmetry with extinctions; $l = 2n + 1$ for the $(h0l)$ projection and $k = 2n + 1$ for the $(0k0)$ line, uniquely characterizing the space group as $P2_1/c$. Least-squares lattice constants were determined from a fit of 18 measurements of the copper $\text{K}\alpha_1$ - $\text{K}\alpha_2$ doublet at $2\theta > 70^\circ$ measured under fine conditions (1° T.O.A. and 0.05° slit). The resultant lattice constants and their estimated standard deviations are:

$$\begin{aligned} a &= 8.657 \pm .001 \text{ \AA} \\ b &= 10.513 \pm .001 \text{ \AA} \\ c &= 10.378 \pm .001 \text{ \AA} \\ \beta &= 99.68 \pm .01^\circ \end{aligned}$$

A calculated density of 1.39 g./c.c assuming four formula weights per unit cell seemed a reasonable value and was later confirmed by the complete structure determination.

Three-dimensional intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using $\text{Cu-K}\alpha$ radiation and balanced nickel and cobalt filters. A total of 1986 unique intensities were measured to a two-theta limit of 120° ($d = 0.889 \text{ \AA}$). Of these, 1479 were considered statistically significant by the criterion (where the sigmas were based entirely on counting statistics)

$$(I_{\text{Ni}} - 2\sigma(I_{\text{Ni}})) - (I_{\text{Co}} + 2\sigma(I_{\text{Co}})) > 100 \text{ counts}$$

(10 second counting times). The intensities were corrected for α_1 - α_2 splitting as a function of two-theta and for absorption as a function of phi (linear $\mu = 24.9 \text{ cm}^{-1}$ and a 19% difference in a phi-scan at $\chi = 90.0^\circ$). Lorentz polarization corrections were made and the intensities were reduced to structure amplitudes in the usual manner.

Structure Determination.

Normalized structure magnitudes, $|E|$'s, were calculated using a K-curve as described by Karle (5). Using all data with $|E| > 1.5$ (240 E's), an origin and two permuting reflections were chosen. Of the four permutations, all run with a probability of .999, the choice that proved correct phased 225 E's and had a consistency index of .944 (6). The E-map generated by this choice contained

TABLE I

Fractional Coordinates and Anisotropic Thermal Parameters (a)
 (Anisotropic Thermal Parameters $\times 10^4$, Estimated Standard Deviations in Parentheses Refer to Last Decimal Place)

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P1	0.1617(1)	0.6435(1)	0.339(1)	151(2)	101(1)	79(1)	68(1)	-7(1)	-26(1)
C2	0.3753(4)	0.6350(3)	0.3384(3)	171(7)	76(4)	91(4)	-11(4)	-27(4)	-16(3)
N3	0.4270(3)	0.5366(3)	0.2547(2)	63(4)	92(3)	69(3)	-8(3)	-7(3)	-4(2)
C4	0.3478(3)	0.5308(3)	0.1163(3)	77(5)	104(4)	64(3)	-21(4)	14(3)	4(3)
N5	0.1797(3)	0.5176(2)	0.1040(2)	59(3)	74(3)	60(3)	-4(3)	0(2)	2(2)
C6	0.1283(4)	0.3977(3)	0.1491(3)	95(5)	83(4)	58(3)	-24(4)	0(3)	1(3)
N7	0.1600(3)	0.3785(3)	0.2921(2)	90(4)	89(3)	62(3)	-1(3)	9(3)	8(2)
C8	0.1087(4)	0.4795(4)	0.3727(3)	91(5)	153(5)	66(3)	34(4)	24(3)	3(3)
C9	0.1057(4)	0.6277(3)	0.1553(3)	121(6)	83(4)	96(4)	42(4)	-2(4)	3(3)
C10	0.5738(4)	0.4951(3)	0.2835(3)	91(5)	106(4)	98(4)	-20(4)	-4(4)	1(3)
N11	0.6981(4)	0.4545(4)	0.3101(3)	97(5)	194(6)	187(5)	20(5)	-33(4)	-6(4)
C12	0.2736(4)	0.3017(3)	0.3477(3)	103(5)	79(4)	75(3)	-14(4)	12(3)	0(3)
N13	0.3673(4)	0.2347(3)	0.3988(3)	213(7)	116(4)	111(4)	59(4)	-10(4)	13(3)

(a) Anisotropic temperature factors of the form: $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

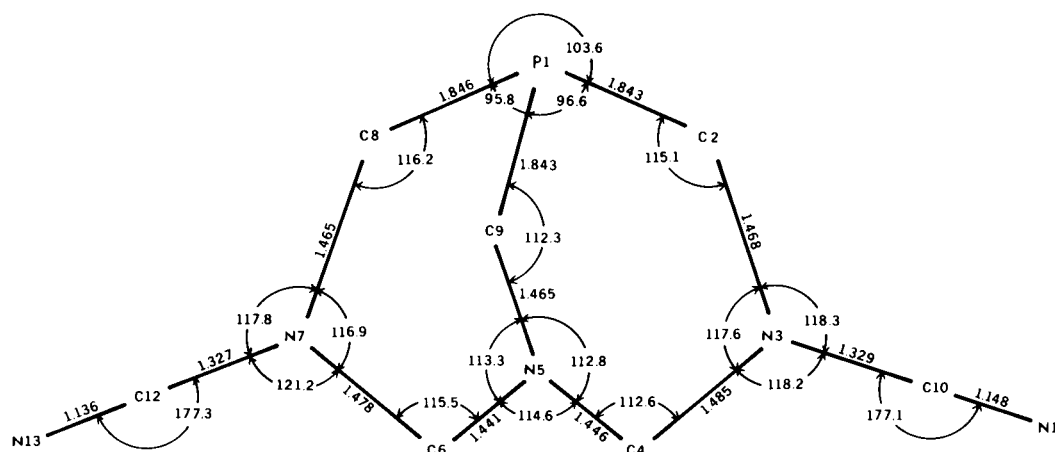


Figure 1. Schematic Drawing of the Molecule with Distances and Angles Indicated.

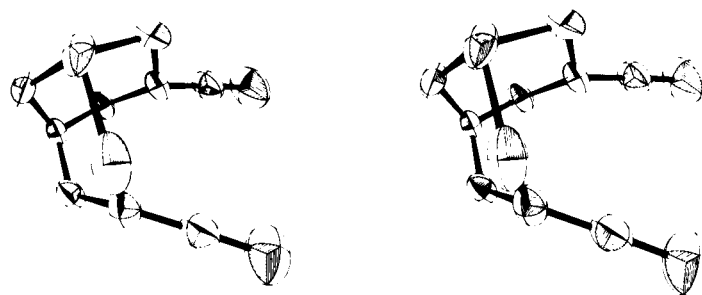


Figure 2. ORTEP Stereodrawing of the Molecule.

TABLE II
Hydrogen Fractional Coordinates

Atom*	X	Y	Z	β
H2	0.4265(34)	0.6143(28)	0.4323(27)	4.1(8)
H2'	0.4084(32)	0.7071(26)	0.3108(26)	3.5(7)
H4	0.4065(39)	0.4593(31)	0.0624(32)	6.6(10)
H4'	0.3767(37)	0.6118(31)	0.0778(30)	5.7(9)
H6	0.1860(38)	0.3182(33)	0.1028(32)	6.7(10)
H6'	-0.0044(35)	0.3926(30)	0.1168(29)	5.4(9)
H8	0.1439(35)	0.4632(28)	0.4634(28)	4.5(8)
H8'	-0.0190(37)	0.4726(30)	0.3517(30)	5.8(9)
H9	-0.0123(30)	0.6142(25)	0.1375(24)	3.0(7)
H9'	0.1333(37)	0.7134(32)	0.1146(31)	6.4(10)

only the thirteen peaks anticipated. Isotropic, block-diagonal least-squares (7) began at $R = 0.28$ and refined to $R = 0.18$. After conversion to anisotropic temperature factors, additional least-squares reduced the residual index to $R = 0.11$. A difference Fourier map was calculated at this stage based upon the phases of the non-hydrogens. All ten hydrogen atoms showed up clearly on the maps at heights ranging from 0.7-0.9 $e/\text{\AA}^3$. The positions corresponded reasonably well with those calculated on the basis of previous chemical prejudices. Inclusion of these hydrogens into the least-squares refinement with non-hydrogens varying anisotropically and hydrogens refined isotropically reduced the value of the index to $R = .052$. At this stage, the shifts of all parameters were less than one-tenth of their respective estimated standard deviations and so the refinement was terminated.

Results and Discussion.

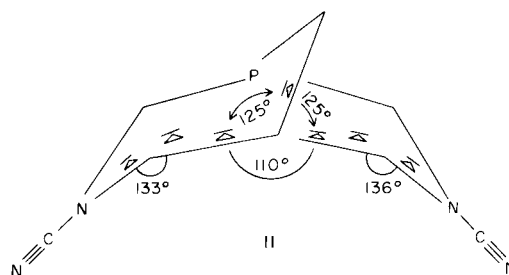
Table I lists the final refined coordinates and anisotropic temperature factors for the non-hydrogen atoms. Table II lists the final refined coordinates and isotropic temperature factors for the hydrogens. Figure 1 is a schematic drawing of the molecule with bond distances and bond angles indicated. Bonds and angles involving P, N, C all have estimated standard deviations (ESD) less than 0.004 \AA and 0.2 $^\circ$, respectively. Bonds and angles involving the hydrogen atoms are significantly higher at 0.04 \AA and 2.5 $^\circ$, respectively.

The compound presents a spectrum of NC bonds, having seven bonds averaging to 1.464 \pm .01 \AA , two bonds averaging to 1.32 $_8 \pm$.01 \AA , two bonds averaging to 1.32 $_8 \pm$.001 \AA and two bonds averaging 1.14 $_2 \pm$.006 \AA . The temptation is strong to label these as single, double and triple bonds, respectively. That the bonding electrons are so localized is evidenced by comparison of these parameters to the presumed standard values for CN bond types of 1.472, 1.322, and 1.153 \AA , respectively (8). Further evidence for the type of hybridization is given by the angles involved. Thus the cyano groups have angles of 177.2 \pm .1 $^\circ$ (*vs.* 180 $^\circ$); the double bonds have angles

averaging to 118.9 \pm 1.2 $^\circ$ (*vs.* 120 $^\circ$); and the single bonds have angles averaging to 115.5 \pm 1.1 $^\circ$ (*vs.* 113-115 $^\circ$ angles found in medium size rings (9)).

The phosphorus-carbon parameters essentially mimic those to be anticipated for 3-covalent phosphorus. Thus the PC distances of 1.844 \pm .002 \AA compare to the 1.841 \pm .003 \AA in trimethylphosphine (10). The CPC angles of the adjacent rings average to 96.2 \pm .4 $^\circ$, slightly less than the literature value (10) of 99.1 $^\circ$ whereas the angle between the rings has opened to 103.6 $^\circ$, slightly more than that value.

The geometry of the molecule itself is most evident in the ORTEP stereodrawing (Figure 2). The sketch of the molecule below (II) shows the dihedral angles which



very closely parallel those expected if two six-membered rings each in the chair form were to share three common atoms (P1, N5 and C9). Surprisingly, the cyano groups together with the three closest atoms are not planar, deviating in each case from planarity by .09 \AA .

Acknowledgments.

The authors wish to express their gratitude to the National Science Foundation (GU-2632) for financial assistance to support this and subsequent studies; to the Department of Health, Education and Welfare for an N.D.E.A. Fellowship (for J.N.B.); and to the computer center at I.S.U.N.O.

REFERENCES

- (1) D. J. Daigle, W. A. Reeves and D. J. Donaldson, *Text. Res. J.*, **40**, 580 (1970).
- (2) D. J. Daigle and A. B. Pepperman, Unpublished but related to work described in British Patent 842,593 (1960) and British Patent 761,985 (1956).
- (3) D. J. Daigle, A. B. Pepperman, Jr. and F. L. Normand, *J. Heterocyclic Chem.*, **9**, 715 (1972).
- (4) L. Hungerford and L. M. Trefonas, *ibid.*, **9**, 347 (1972).
- (5) J. Karle, H. Hauptman and C. L. Christ, *Acta Cryst.*, **11**, 757 (1958).
- (6) J. N. Brown, LSUNO Thesis (1972). Program FAZC, in partial fulfillment of the requirements for a Ph.D.
- (7) Scattering factors for Hydrogen Atoms are from: R.

Stewart, E. Davidson and W. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). All other scattering factors are from: D. Cromer and J. Waber, *Acta Cryst.*, **18**, 104 (1965). The Block Diagonal Least-Squares Program is BDLS and σ^2 weights were utilized throughout. The reliability index cited (R) is the conventional one.

(8) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958; Supplement, 1964.

(9) Compare to Structures containing eight, ten, twelve-membered rings in these papers: (a) L. M. Trefonas and R. Majeste, *Tetrahedron*, **19**, 929 (1963); (b) H. Zacharis and L. M. Trefonas, *J. Heterocyclic Chem.*, **7**, 755 (1970); (c) L. M. Trefonas and J. Couvillion, *J. Am. Chem. Soc.*, **85**, 3184 (1963). (d) L. M. Trefonas, R. Towns and R. Majeste, *J. Heterocyclic Chem.*, **4**, 511 (1967).

(10) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).