

The Crystal and Molecular Structure of 2-(2',4'-Dinitrobenzyl)pyridine*

BY KARL SEFF† AND KENNETH N. TRUEBLOOD

Department of Chemistry, University of California, Los Angeles, California 90024, U.S.A.

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When the pale yellow crystals of 2-(2',4'-dinitrobenzyl)pyridine (DNBP, $C_6H_3(NO_2)_2CH_2C_5NH_4$) are irradiated with light of wavelength 4000 Å or less, a deep blue substance is produced by what is believed to be a reversible tautomeric reaction. The half-life of the excited form is several hours in the crystal but only a few seconds, or much less, in various solvents. Crystals of the isomeric 4-substituted compound do not show this long half-life. DNBP forms monoclinic crystals in space group $P2_1/c$, with $a_0 = 10.276$, $b_0 = 15.198$, $c_0 = 7.708$ Å, $\beta = 101.84^\circ$, and with four molecules in the unit cell. Nearly complete integrated Weissenberg film data were collected with the use of Cu $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least squares to $R = 0.073$. Small corrections for molecular libration are included in the final geometry. The intramolecular angle between the planes of the two aromatic rings is 114° . The closest approach of a methylene hydrogen atom to an electronegative atom is intramolecular to an oxygen atom (at 2.4 Å) on the *o*-nitro group. This nitro group is rotated 32° from the plane of the benzyl ring; the other is twisted 12° from the benzyl plane. These nitro groups undergo appreciable torsional oscillation about the C–N bonds, with approximate libration amplitudes of 8° and 10° . The shortest intermolecular distance from a methylene hydrogen atom to an electronegative atom is 2.6 Å (H...O).

Introduction

When the pale yellow crystals of 2-(2',4'-dinitrobenzyl)pyridine, $C_{12}H_9N_3O_4$, also referred to as α -DNBP or DNBP, are irradiated with light of wavelength 4000 Å or less, a deep blue substance is produced by a reversible tautomeric reaction (Hardwick, Mosher & Passailaigue, 1960). The half-life of the excited form is several hours in the crystal, but only a few seconds or much less in various solvents. The related compound (γ -DNBP) with the pyridine nitrogen atom *para* rather than *ortho* to the dinitrobenzyl group does not show this high solid-state tautomeric stability (Mosher, Hardwick & Ben-Hur, 1962). It has been shown that the presence of a *p*-nitro group on each phenyl ring in diphenylmethane lowers the pK_A of the methylene hydrogen atoms from 30.2 (Steiner & Gilbert, 1965; Steiner & Starkey, 1967) to 15.85 (Bowden & Stewart, 1965). In DNBP the methylene hydrogen atoms are, therefore, presumably the most acidic hydrogen atoms in the structure, and the most likely to be involved in the tautomerization reaction.

We hoped that the determination of the structure would indicate whether the reaction is inter- or intramolecular, and that a mechanism might become apparent. An examination of non-bonded distances in the structure suggests that the tautomerization is probably intramolecular, and that the reaction begins with the transfer of a methylene hydrogen atom to an oxygen of the *o*-nitro group, leaving the two rings interconjugated and shifting the absorption maximum to

longer wavelengths. This hydrogen atom might then be transferred intramolecularly to the pyridine nitrogen atom.

Experimental

Crystals of DNBP (supplied by R. Hardwick and D. Ben-Hur) are either bipyramidal (**b**) or long prismatic (**c**), and are yellow in color, becoming blue upon exposure to fluorescent room light or sunlight. The space group $P2_1/c$, was assigned on the basis of Weissenberg photographs ($h0l$, $l=2n$; $0k0$, $k=2n$). Unit-cell dimensions are: $a_0 = 10.276 \pm 0.002$, $b_0 = 15.198 \pm 0.003$, $c_0 = 7.708 \pm 0.003$ Å, and $\beta = 101.84 \pm 0.02^\circ$; these were determined by a least-squares refinement of fifty-two 2θ values measured on $h0l$ and $hk0$ Weissenberg photographs calibrated with reflections from a quartz sample. The measured density of 1.454 agrees well with the value of 1.460 g.cm⁻³ calculated for a four-molecule unit cell. The intensities of 2563 independent reflections (about 95% of the Cu sphere) were measured with a densitometer from integrated Weissenberg films of the layers 0 to 14 along **b** and 0 to 6 along **c**; the intensities of 2120 of these were above the minimum observable limit. Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å), reasonably monochromatized by means of a $K\beta$ filter, was used throughout. Small spherical absorption corrections ($\mu = 9.67$ cm⁻¹) were made assuming approximate crystal radii of 0.02 cm for the bipyramid ($0.02 \times 0.03 \times 0.02$ cm) mounted about **b**, and 0.02 cm for the prism ($0.02 \times 0.025 \times 0.04$ cm) mounted about **c**.

Some weak reflections on the **b**-axis photographs were observed to be markedly more intense than the same reflections observed about **c**. The conditions about **b** (equi-inclination Weissenberg photographs taken about an axis normal to a reciprocal net) are

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† Present address: Department of Chemistry, University of Hawaii, Honolulu, Hawaii, 96822.

Table 1. Observed and calculated structure factors

The running index is h; values of k and l for each group immediately precede that group. The central column is 10|F0|, the right-hand column 10Fc. The F0 listed for unobserved reflections is 1.48 Fmin. The symbols immediately following some values of F0 have these meanings: U, unobserved; E, suffers from extinction but included in least-squares; *, inaccurate observation (only 1,0,0) but included in least-squares.

Table with multiple columns containing numerical data and symbols (e.g., U, E, *) representing observed and calculated structure factors for various groups.

Table 2. *Final positional parameters and their standard deviations*

Values given are $\times 10^4$ for C, N and O and $\times 10^3$ for H. See Fig. 1 for the identities of the atoms. The e.s.d., separated by a comma, is in the units of the least significant digit given for the corresponding parameter.

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$
C(1)	1934,2	5200,1	-1903,3
C(2)	1277,3	5982,2	-2448,4
C(3)	1078,3	6220,2	-4208,4
C(4)	1552,3	5690,2	-5377,4
C(5)	2187,4	4936,2	-4724,4
N(1)	2389,2	4676,1	-3027,3
C(6)	2197,3	4953,2	41,3
C(7)	3055,2	4145,1	507,3
C(8)	2694,2	3292,1	-43,3
C(9)	3518,2	2572,2	426,3
C(10)	4732,2	2724,2	1528,3
C(11)	5142,3	3550,2	2116,4
C(12)	4308,2	4248,2	1591,4
N(2)	1378,2	3092,1	-1152,3
O(1)	437,2	3540,2	-958,3
O(2)	1300,2	2479,2	-2179,3
N(3)	5600,2	1965,2	2106,4
O(3)	5315,3	1258,2	1362,4
O(4)	6546,3	2078,2	3303,4
H(1)	99,4	642,2	-152,6
H(2)	53,4	677,2	-473,5
H(3)	140,3	590,2	-664,5
H(4)	250,5	459,3	-578,7
H(5)	130,3	489,2	32,4
H(6)	276,3	544,2	89,5
H(7)	323,3	198,2	6,4
H(8)	588,4	357,3	274,5
H(9)	474,3	484,2	190,4

were about 0.05 e.s.d.'s of position; no non-hydrogen coordinate shift exceeded 0.0006 Å, or 0.2σ, and no hydrogen coordinate shift exceeded 0.01 Å, or 0.2σ. Table 1 gives the observed and calculated structure factors. The final positional and thermal parameters are listed in Tables 2 and 3 respectively. Two regions of negative residual electron density, with minimum values of -0.42 and -0.44 e.Å⁻³, occurred in a final difference Fourier synthesis at the positions of the two nitro nitrogen atoms. Without a more detailed analysis of the difference map, and of possible variation of the *f* curve for nitrogen as a parameter in the least-squares, the significance of this finding with regard to possible electron withdrawal from the nitrogen atoms remains uncertain. Otherwise, the highest and lowest points on this map were +0.25 and -0.27 e.Å⁻³, about three times the e.s.d. of the electron density, 0.08 e.Å⁻³.

Thermal motion

The motions of several different groups of atoms have been analyzed in terms of the rigid-body tensors of translation (T), libration (L), and screw motion (S) (Schomaker & Trueblood, 1968). The computer program used was ACA(new)No. 1. The r.m.s. discrepancy between observed and calculated U_{ij} serves as a measure of the applicability of the analysis and thus of the rigidity of a particular grouping.

Table 3. *Thermal vibration parameters and their standard deviations*

The *b* are $\times 10^4$. See Fig. 1 for the identities of the atoms. The e.s.d., separated by a comma, is in the units of the least significant digit given for the corresponding parameter.

I. Carbon, nitrogen, or oxygen temperature factor =

$$\exp \{ -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \}$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	91,2	38,1	167,4	11,2	35,4	8,3
C(2)	137,3	49,1	238,6	54,3	107,6	28,4
C(3)	125,3	62,2	243,7	64,3	65,6	83,5
C(4)	131,3	58,1	193,5	21,3	38,6	47,4
C(5)	192,4	57,1	162,5	40,4	100,7	21,4
N(1)	156,3	43,1	153,4	34,2	67,5	14,3
C(6)	131,3	42,1	166,5	28,3	49,5	-11,3
C(7)	102,2	38,1	144,4	4,2	53,4	1,3
C(8)	89,2	41,1	146,4	-11,2	54,4	-1,3
C(9)	112,2	35,1	197,5	-10,2	98,5	3,3
C(10)	103,2	40,1	194,5	20,2	75,5	39,3
C(11)	101,2	51,1	189,5	-9,2	6,5	22,3
C(12)	120,3	37,1	196,5	-13,2	7,5	-10,3
N(2)	96,2	51,1	183,4	-27,2	51,4	-12,3
O(1)	99,2	69,1	265,5	12,2	18,4	1,3
O(2)	136,3	85,1	290,6	-73,3	68,5	-142,4
N(3)	125,3	53,1	263,6	36,3	92,6	82,4
O(3)	202,3	45,1	375,7	56,3	167,7	43,4
O(4)	181,4	77,2	405,8	83,4	-63,8	79,5

II. Hydrogen

	B (Å ²)		B (Å ²)
H(1)	6.9,9	H(6)	5.4,7
H(2)	6.1,8	H(7)	4.7,6
H(3)	5.0,7	H(8)	6.8,10
H(4)	8.4,11	H(9)	4.9,6
H(5)	4.8,6		

Some rigid-body parameters for the pyridine ring with the methylene carbon atom included are given in Table 4; the fit is good. The translational motion is reasonably isotropic, while libration is quite anisotropic, with the primary motion corresponding to a r.m.s. amplitude of 9.5° about an axis ($L1$) 14° away from the exocyclic C-C bond. The secondary libration has a 4° r.m.s. amplitude about an axis ($L2$) which makes a 4° angle with the pyridine ring plane (Table 5) and an 84° angle with the exocyclic C-C bond. Substantially the same motion is indicated by the analysis of the six-atom pyridine ring alone.

Three rigid-body analyses were done for the dinitrobenzyl group. One of these analyses included only the ring and the methylene carbon atom; the second

also included both nitro nitrogen atoms and indicated approximately the same motion and rigidity as the first. In the third analysis, the nitro oxygen atoms were included as well; this entire group of atoms did not comprise a satisfactorily rigid body, which is not surprising in view of the known high torsional oscillations of aromatic nitro groups (Trueblood, Goldish & Donohue, 1961). Translational motions are nearly isotropic.

These motions of the nitro groups were best examined by subtracting the calculated U_{ij} corresponding to the rigid body motion of the dinitrobenzyl group without oxygen atoms (C_7N_2) from the observed U_{ij} of the entire dinitrobenzyl group ($C_7N_2O_4$). The four oxygen atoms show residual r.m.s. displacements corresponding to libration amplitudes of 10° , 7° , 6° , and

Table 4. *Rigid-body thermal parameters*

Axes of reference are **a, b, c***. E.s.d. of components of **L** are given after them, separated by a comma, in units of last place shown.

$L[\times 10^{-1}(\text{e})^2]$	Pyridine ring and methylene C: N(1), C(1) to C(5), and C(6)			Benzyl group: C(7) to C(12), and C(6)		
	110,13	-11,14 290,21	-78,24 -306,23 742,52	184,33	-82,25 92,50	32,22 -82,22 174,20
<i>Principal axes of L</i>						
	r.m.s. amplitude	Direction cosines ($\times 10^3$)		r.m.s. amplitude	Direction cosines ($\times 10^3$)	
$L1$	9.5°	082	445 -892	5.3°	626 -521	580
$L2$	4.1	580	-749 -321	3.8	694 033	-719
$L3$	2.7	811	491 319	1.4	356 853	382
<i>Principal axes of reduced† T</i>						
	r.m.s. amplitude	Direction cosines ($\times 10^3$)		r.m.s. amplitude	Direction cosines ($\times 10^3$)	
	0.23 \AA	764	537 -358	0.22 \AA	-789 419	-449
	0.21	095	-642 -761	0.20	327 905	271
	0.20	-638	547 -542	0.20	520 066	-851
<i>Displacement of libration axes from intersecting (Å)</i>						
Parallel to $L1$		-1.19			2.94	
Parallel to $L2$		-1.11			0.49	
Parallel to $L3$		-0.34			-0.75	
<i>Effective screw translations (Å)</i>						
Parallel to $L1$		0.001			-0.003	
Parallel to $L2$		-0.028			0.022	
Parallel to $L3$		0.040			-0.048	
$(\Delta U_{ij})^\ddagger$ (Å ²)		0.0014			0.0016	

† Corresponding to equation (20) of Schomaker & Trueblood (1968).

Table 5. *Least-squares planes†*

No.	Direction cosines ($\times 10^4$) with respect to			Description of plane‡	r.m.s. deviation from plane (Å $\times 10^3$)
	a	b	c *		
1	8507	4906	1890	C_5N (pyridine ring)	4
2	5795	1336	-8040	C_6 (benzyl ring)	7
3	3326	6260	-7054	CNO_2 (<i>o</i> -nitro group)	4
4	7086	2364	-6648	CNO_2 (<i>p</i> -nitro group)	2

† For the molecule whose coordinates are given in Table 2.

‡ See Table 6 also.

14° for O(1), O(2), O(3), and O(4) respectively, as measured normal to the plane of the appropriate nitro group. The averages of these for each nitro group give approximate r.m.s. librations of 8° and 10° about the respective C-N bonds. These torsional oscillations are comparable to but slightly smaller than those in other aromatic nitro compounds. For example, in 4-nitroaniline (Trueblood, Goldish & Donohue, 1961) an r.m.s. amplitude of 13° is found at room temperature, and in 3-nitroperchlorylbenzene (Palenik, Donohue & Trueblood, 1968) the amplitude is 14° .

The bond lengths and angles were corrected (Cruickshank, 1956, 1961) for the effects of thermal motion indicated by the above rigid-body analyses. (The N-O bond distances were corrected by the method of Busing & Levy (1964), assuming 'riding' motion.) The molecular geometry is given in Fig. 1, Fig. 2, and Table 7.

Crystal and molecular structure

The direction cosines of the least-squares planes of each ring and each C-NO₂ group are presented in Table 5, and the displacements of some atoms from these planes in Table 6. No atom used to define a plane deviates significantly from that plane. The intramolecular angle between the planes of the two aromatic rings is 114° . Since the nitro nitrogen atoms are about 0.05 Å out of the plane of the benzyl ring, the angles between the nitro group planes and the plane of the benzyl ring do not represent precisely the angles of twist about the C-N bonds, but they are sufficient for our discussion. The *o*-nitro group [N(2), O(1) and O(2)] is twisted approximately 32° (Fig. 2) from the benzyl plane, and the *p*-nitro group [N(3), O(3) and O(4)] is twisted 12° in the opposite sense. The C(1)-C(6) bond

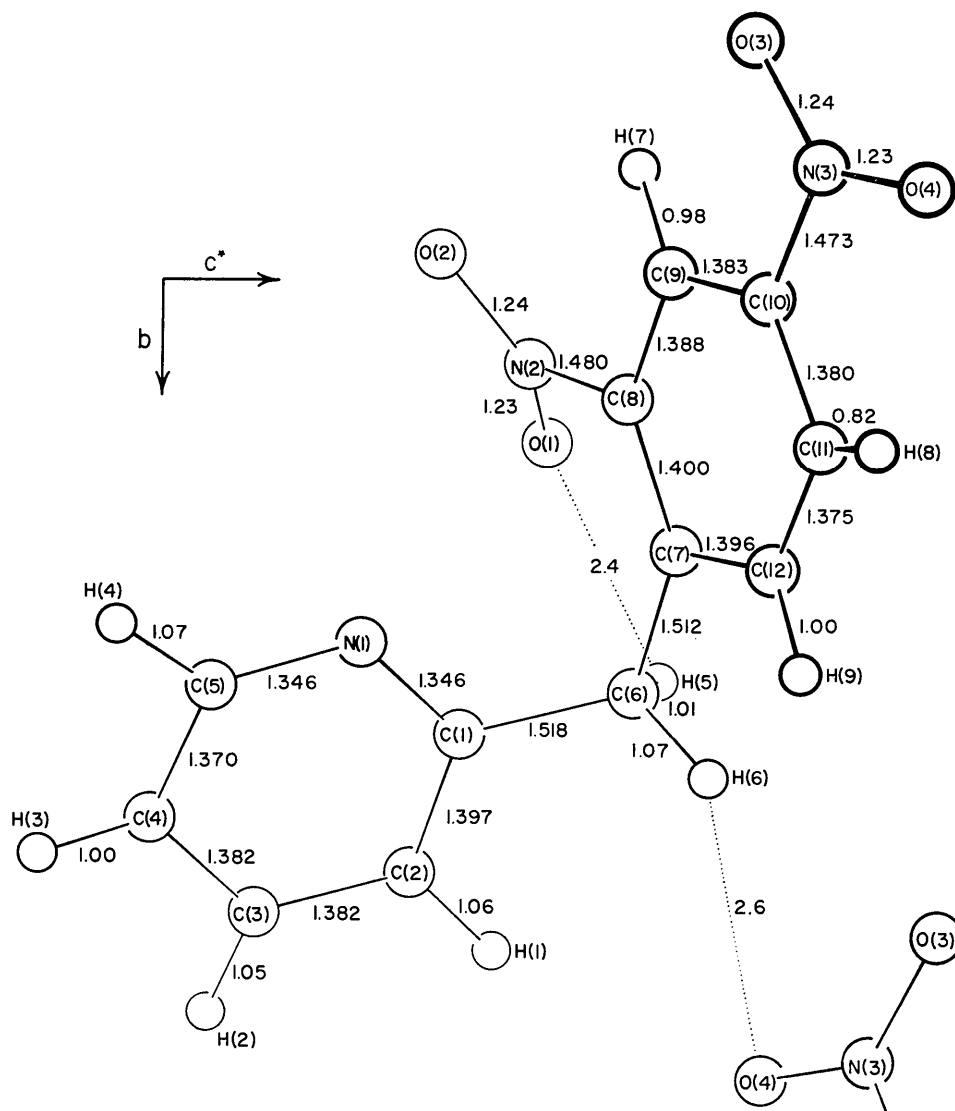


Fig. 1. Bond lengths and the two shortest methylene-hydrogen to nitro-oxygen distances.

makes an angle of 37° with the plane of the benzyl ring.

The molecular geometry of DNBP appears to be in agreement with previous findings on related compounds. The benzyl ring C-C distances average 1.387 \AA with an r.m.s. deviation of 0.009 \AA , in agreement with values of 1.390 \AA in the tetraphenylphosphonium ion (Goldstein, Seff & Trueblood, 1968), 1.389 \AA in [3.3]paracyclophane (Gantzel & Trueblood, 1965), and 1.392 \AA in benzene (Cox, Cruickshank & Smith, 1958). The pyridine ring has C-C distances of 1.383 \AA with an r.m.s. deviation of 0.010 \AA and C-N distances of 1.346 \AA . These compare well with values (uncorrected for libration) of 1.388 and 1.342 in 1,2-di-(2-pyridyl)ethenediol-1,2 (Ashida, Hirokawa & Okaya, 1965) and 1.380 and 1.349 in 1-phenyl-2-(2-pyridyl)ethanedione-1,2 (Ashida, Hirokawa & Okaya, 1966).

The C-C-C angle at the methylene carbon atom is 114.4° (with an e.s.d. of 0.4°), somewhat larger than

the value 111.5° (1.0°) found in a 2,2'-methylenedi-quinoline (Thuijl & Romers, 1966) and the values of 112.4° (0.2°) in propane (Lide, 1960) and of 112.4° (0.3°) in n-butane (Bonham & Bartell, 1959). The C-N bonds at the nitro group average 1.476 \AA with an r.m.s. deviation of 0.004 \AA , and the N-O bonds are 1.235 \AA with an r.m.s. deviation of 0.005 \AA . In 4-nitroaniline (Trueblood, Goldish & Donohue, 1961) these bond lengths were found to be 1.460 and 1.246 \AA respectively. The C-N bond lengths in the present molecule are near the average of 1.48 \AA found for a number of nitro-aromatic hydrocarbons (Trotter, 1960).

Some non-bonded approach distances are given in Table 8, and two of these are shown in Fig. 1. Interactions between methylene hydrogen atoms and electronegative atoms are of particular interest in connection with the tautomeric reaction; the shortest of these are the H(5) to O(1) intramolecular contact of 2.4 \AA and the intermolecular H(6) to O(4) distance of 2.6 \AA (Fig. 1). These are approximately the same as the intra-

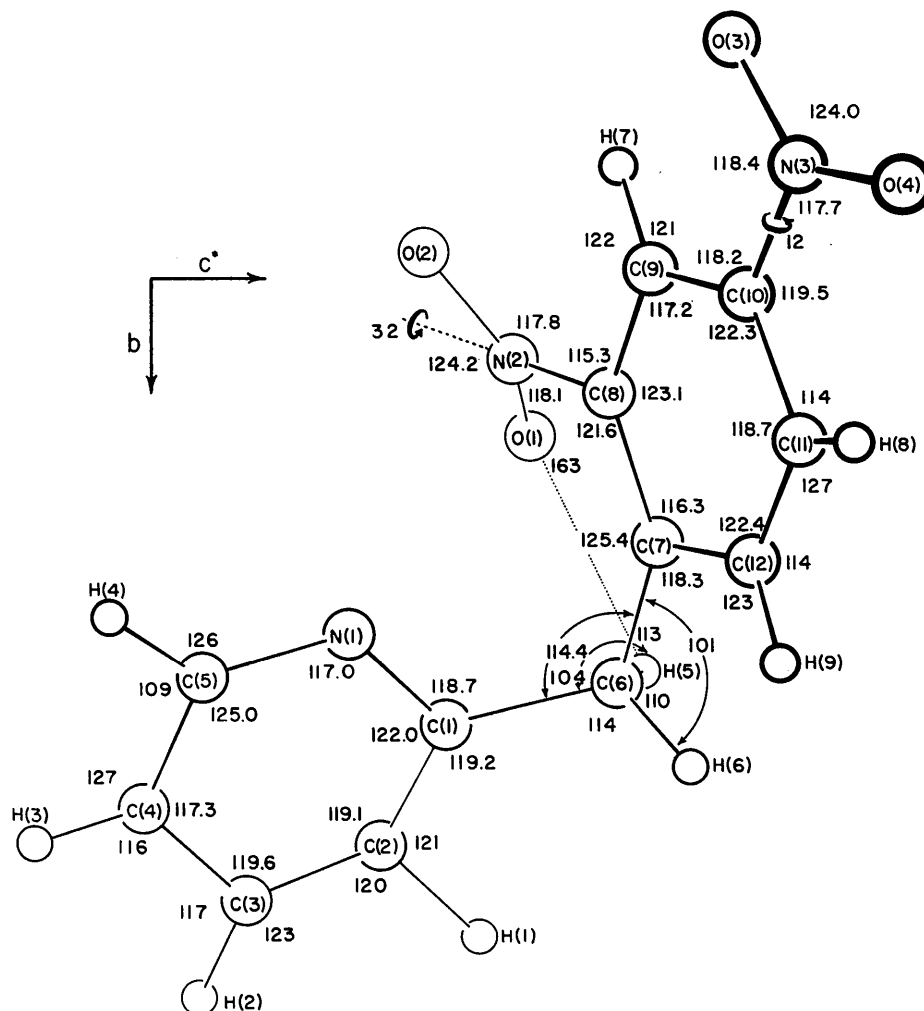


Fig. 2. Bond and torsion angles.

molecular O...H distances found between nitro oxygen atoms and aromatic hydrogen atoms at adjacent ring positions on the dinitrobenzyl group. The 32°-twist of the *o*-nitro group from the plane of the benzyl group results in a close intramolecular non-bonded approach of O(1) to the pyridine nitrogen N(1) (3.3 Å) as well as to H(5). The large librational motions of the *o*-nitro group and of the pyridine ring presumably result in some appreciably closer instantaneous approaches (unless these two motions happen to be strongly coupled and of the same frequency).

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Table 6. Deviations of atoms from least-squares planes (Å × 10³)

See also Table 5. Boldface deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table 2 lies between that plane and the origin. See Fig. 1 for the identities of the atoms.

Atom	Plane No.	Atom	Plane No.		
	1		2	3	4
N(1)	-2	C(1)	-1227		
C(1)	0	C(6)	24		
C(2)	5	C(7)	2	-612	
C(3)	-6	C(8)	7	2	
C(4)	3	C(9)	-10	679	263
C(5)	1	C(10)	5		1
C(6)	61	C(11)	4		-234
C(7)	213	C(12)	-8		
H(1)	85	N(2)	56	-7	
H(2)	-73	O(1)	662	2	
H(3)	15	O(2)	-489	2	
H(4)	13	N(3)	46		-4
H(5)	-774	O(3)	-160		1
H(6)	916	O(4)	296		1
		H(5)	766		
		H(6)	187		
		H(7)	22		
		H(8)	-8		
		H(9)	-164		

Table 7. Bond lengths* (Å)

Atoms	Distance		Atoms	Distance	
	Uncorrected	Corrected†		Uncorrected	Corrected†
C(1)—C(2)	1.389	1.397	C(8)—N(2)	1.476	1.480
C(2)—C(3)	1.378	1.382	C(10)—N(3)	1.469	1.473
C(3)—C(4)	1.370	1.382	N(2)—O(1)	1.217	1.23‡
C(4)—C(5)	1.364	1.370	N(2)—O(2)	1.214	1.24‡
C(5)—N(1)	1.342	1.346	N(3)—O(3)	1.226	1.24‡
N(1)—C(1)	1.331	1.346	N(3)—O(4)	1.208	1.23‡
C(1)—C(6)	1.515	1.518	H(1)—C(2)	1.06	
C(6)—C(7)	1.511	1.512	H(2)—C(3)	1.04	
C(7)—C(8)	1.392	1.400	H(3)—C(4)	1.00	
C(8)—C(9)	1.384	1.388	H(4)—C(5)	1.07	
C(9)—C(10)	1.377	1.383	H(5)—C(6)	1.07	
C(10)—C(11)	1.372	1.380	H(6)—C(6)	1.00	
C(11)—C(12)	1.372	1.375	H(7)—C(9)	0.99	
C(12)—C(7)	1.392	1.396	H(8)—C(11)	0.82	
			H(9)—C(12)	1.00	

* Estimated standard deviations (not including an expected error arising from the use of spherically symmetric form factors) average: C—C, 0.005 Å; N—O, 0.01 Å; C—H, 0.04 Å; angles involving heavy atoms, 0.4°; angles involving one H, 3°. All bond angles are shown in Fig. 2.

† The shape parameters (q^2) (Cruickshank, 1956, 1961) used in calculating bond-length corrections were as follows: aromatic C, 0.08; aliphatic C, 0.096; aromatic N, 0.069; nitro N, 0.075.

‡ Corrected on the assumption of riding motion, (Busing & Levy, 1964).

Table 8. *Some non-bonded interatomic distances**

(a) Intramolecular				
	O(1)····N(1)	3·30 Å	O(1)····H(5)	2·4 Å
	····C(1)	3·12	O(2)····H(7)	2·5
	····C(6)	2·81	O(3)····H(7)	2·4
	N(1)····N(2)	3·10	O(4)····H(8)	2·4
	····C(7)	2·78	N(1)····H(5)	3·0
	····C(8)	3·08	····H(6)	3·2
			N(2)····H(5)	3·0
(b) Intermolecular†				
$(x, \frac{1}{2}-y, -\frac{1}{2}+z)$	O(2)····O(1)	3·26 Å	O(2)····C(9)	3·22 Å
	N(1)····O(3)	3·44	O(3)····C(11)	3·25
	C(10)····O(4)	3·41	H(8)····O(3)	3·0
	O(2)····N(2)	3·20	H(4)····H(7)	2·5
	····C(8)	3·10		
$(-x, \frac{1}{2}+y, -\frac{1}{2}-z)$	C(2)····O(2)	3·46	H(2)····O(1)	2·9
	C(3)····O(2)	3·44	····O(2)	2·8
	H(1)····O(2)	2·9	····N(2)	3·0
$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	H(6)····O(3)	2·9	H(6)····N(3)	3·1
	····O(4)	2·6	H(9)····O(3)	2·5
$(x, y, -1+z)$	H(3)····H(5)	2·8	H(4)····H(6)	2·9
	····H(6)	2·7		
$(-x, 1-y, -1-z)$	O(1)····C(4)	3·34	H(2)····O(2)	2·9
	H(3)····O(1)	2·5		
$(-x, 1-y, -z)$	H(1)····O(1)	2·6	H(5)····H(5)	2·6
	H(5)····O(1)	3·1		
$(1-x, 1-y, -z)$	H(9)····N(1)	3·0	H(8)····C(2)	3·0
$(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	O(3)····C(12)	3·42		

* Some *intramolecular* distances and all *intermolecular* distances less than the following are given: H···H, 2·7 Å; H···C, N, O, 3·1 Å; C, N, O···C, N, O, 3·5 Å. These limits are increased by 0·2 Å for distances involving H(5) and H(6).

† The first atom of each pair has coordinates as given in Table 2. The second atom is related to the one in Table 2 by the symmetry operation given in the subheading.

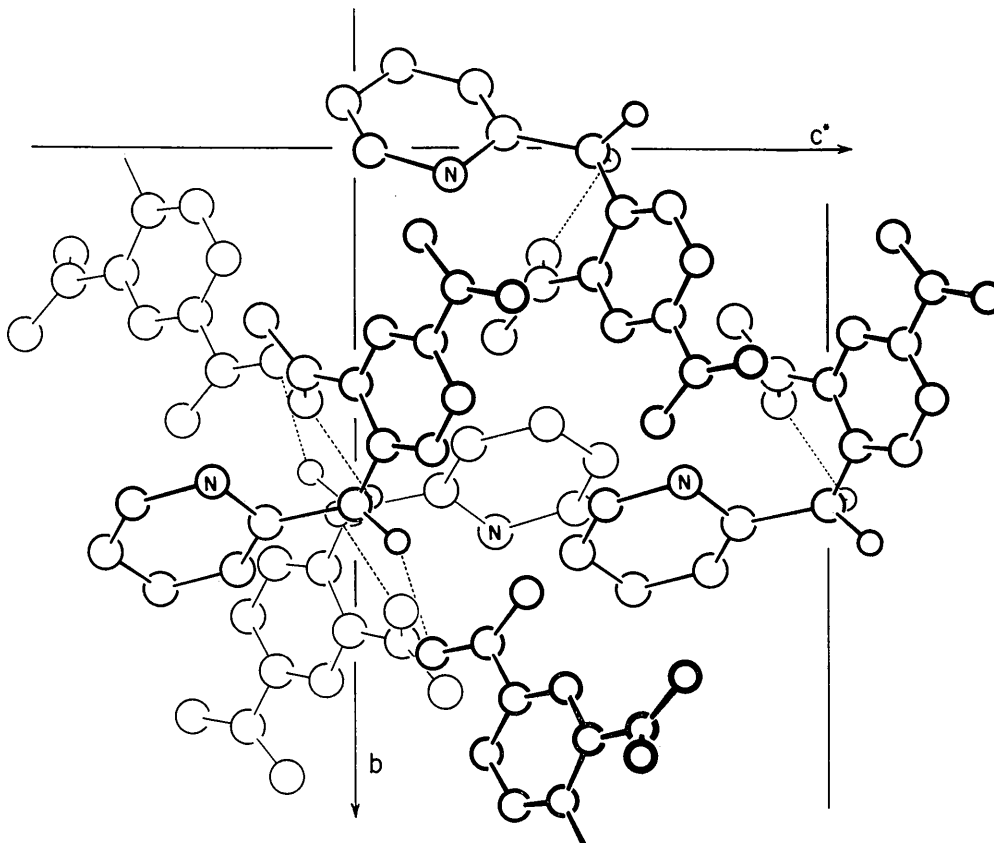


Fig. 3. The arrangement of DNBP molecules in the structure.

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The Geometrical Factor in the Crystal Chemistry of Metals: Near-Neighbour Diagrams

BY W. B. PEARSON

Division of Pure Physics, National Research Council of Canada, Ottawa, Canada

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In an attempt to gain some quantitative assessment of the influence of the geometrical principles of Laves for the structures of metals on the occurrence of phases, and on their structural dimensions, a model has been adopted that allows the atoms to be compressed until successively $A-A$, $A-B$ and $B-B$ contacts are formed. The 'near-neighbour diagrams' that are obtained are thus more suitable for metals than the space filling diagrams of Laves, which are based on an incompressible atom model. They permit an assessment of (1) the relative importance of coordination, and geometrical and bond factors with regard to the occurrence of phases as a function of radius ratio of the component atoms and (2) the influence of these factors on the unit-cell dimensions and atomic parameters of phases with a given structure. The quantitative aspect is introduced by comparing the actual structural dimensions of phases having a given structure, with interatomic separations permitted by the structural geometry.

Introduction

The geometrical principles of Laves (1956), that the structures of metals, in the absence of other dominant effects such as bond factors, should exhibit the highest degree of space filling, the highest symmetry and the greatest number of connexions between the atoms, have been a conversation piece for a decade. However, the difficulty in explicitly analysing the relative importance of these geometrical effects in structures is that they are amenable to discussion rather than quantitative measurement. Although Laves himself did introduce a space filling model for binary systems to compare the relative favourability of various structures at different radius ratios of the component atoms, it appears to be inappropriate for metals since it is based on a hard-sphere model of the atom, whereas one of the main properties of metals is the compressibility of

the atoms. Furthermore, the space filling model as presented by Laves and extended by Parthé (1961) only compares *structures* and does not examine the *dimensional behaviour of phases with given structures*; also it has obvious difficulties of application to complex structures where many different atomic contacts may occur.

In order to examine in a more quantitative manner the geometrical influence on structure type, and the structural dimensions of phases with a given structure, we develop a model that permits the atoms to be compressed in order to realize successively all of the different $A-A$, $A-B$ etc. contacts permitted by the geometry of the structure. The conditions for the formation of the various atomic contacts are satisfied by straight lines on the 'near-neighbour diagrams' (n.n.d.) which are obtained. The known lattice and atomic parameters of phases with a given structure permit