der Literatur angegebenen Werten überein (Davies & Corbridge, 1958; Corbridge, 1960, Eanes & Ondik, 1962).

Die Abstände Phosphor-Sauerstoffatom der freien Ecken P–O (→ *M*) ergeben einen mittleren Wert von 1,49 Å, wenn der Abstand P–(1) nicht berücksichtigt wird. Dieser relativ grosse Wert kommt dadurch zustande, dass ein Teil der O-Atome an Wasserstoffbrückenbindungen beteiligt ist. Der Abstand P–(1) unterscheidet sich mit 1,70 Å wesentlich von allen übrigen und ist nur dadurch zu erklären, dass die Lage (1) vom Stickstoffatom besetzt ist.

Angaben über P–NH_2-Abstände sind in der Literatur verhältnismässig wenig zu finden. Der von Hobbs, Corbridge & Raistrick (1953) und von Cruickshank (1961, 1964) verfeinerte P–N-Abstand für $NaPO_3NH_3$ von 1,769 ± 0,019 Å bezieht sich auf eine P–N-Einfachbindung.

Die Kaliumatome K(2), K(3), K(4) sind von 7 O-Atomen, K(1) von 6 O-Atomen und einem N-Atom mit einem mittleren Abstand von 2,86 Å umgeben (Fig. 5). Der längste Abstand ergibt sich mit 3,18 Å für Kalium-Stickstoff, K(1)–(1).

Von den berechneten intermolekularen Abständen sind die kürzesten Abstände für O–O und N–O in Fig. 6 angegeben. Während die O–O-Abstände durch ihre Grösse auf mehr oder weniger starke Wasserstoffbrückenbindungen hinweisen, sind die N–O-Abstände so gross, dass man höchstens mit schwachen Wasserstoffbrückenbindungen rechnen kann.

Man sollte erwarten, dass bei gleichzeitigem Vorliegen von Aminogruppen und Wasser starke N · · · H · · · O-Brücken ausgebildet werden. Da dies nicht der Fall ist, kann man annehmen, dass die Anionen durch die zahlreichen O · · · H · · · O-Brücken und die Koordination zum Kalium in eine solche Lage gebracht werden, dass das N-Atom räumlich ungünstig für die Ausbildung von Wasserstoffbrückenbindungen liegt.

In der Elektronendichte-Projektion $\varrho(y, z)$ [Fig. 2(*b*)] fällt die Anordnung der Sauerstoffatome 11, 12, 13, 14 auf, die den Wassermolekülen entsprechen. Die Lagen der H-Atome konnten auch nach den $(F_o - F_c)$-Synthesen nicht lokalisiert werden. Es ergibt sich damit für das Gesamtbild der Struktur eine abwechselnde Folge von Schichten aus $P_3O_9NH_2$-Anionen mit Schichten aus Wasser.

Herrn Prof. Thilo danke ich für sein Interesse an dieser Arbeit, ebenso danke ich Herrn Dr Jost für wertvolle Diskussionen und Fräulein Jutta Bethge für die Durchführung von Rechenarbeiten.

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Crystal, Molecular and Electronic Structure of *p*-Nitrophenyl Azide

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Crystals of *p*-nitrophenyl azide at 100 °K are orthorhombic, $a = 18{\cdot}05$, $b = 10{\cdot}29$, $c = 3{\cdot}73$ Å, space group $P2_12_12_1$, with four molecules in the unit cell. The previously determined structure has been refined by three-dimensional differential syntheses. Values of the bond lengths, bond angles and intermolecular distances are given and compared with Hückel molecular orbital results.

Introduction

In methyl azide (Livingston & Rao, 1960), in hydrogen azide (Amble & Dailey, 1950) and in cyanuric triazide (Hughes, 1935; Knaggs, 1935) the N_3 chain is linear and the R–N=N angle lies in the range 110°–120°. Therefore it is probable that the same geometrical features will appear when the N_3 chain is attached to

a phenyl ring. Simple molecular-orbital theory can be used to predict the relative stability of different geometries in nitrogen chains (Roberts, 1961). Using the values $\alpha_N=\alpha_C+0{\cdot}5\beta$, $\alpha_O=\alpha_C+\beta$, and all the nearest neighbours exchange integrals equal to β, the results shown in Table 1 were obtained.

For all the molecules configuration (II) is, on the average, the most stable. To confirm this result by an X-ray structure determination, *p*-nitrophenyl azide has been chosen. This substance melts at 72°C, and therefore after a preliminary room temperature two-dimensional study (Mugnoli, Mariani & Simonetta, 1962; Mugnoli & Mariani, 1964) the complete structure determination and refinement has been carried out at low temperature.

Experimental

p-Nitrophenyl azide crystallizes from light petroleum in the form of elongated orthorhombic tablets, bounded by {100} and {010} pinacoids. The crystals are sensitive to light and to prolonged X-ray exposure. A similar behaviour has been observed in several inorganic azides (Krause, 1961, 1963). The density, determined by the flotation method, is 1·50 g.cm^{-3} at room temperature. Single-crystal X-ray diffraction data were collected with Cu $K\alpha$ radiation at 100 ± 5°K. The crystal was sealed in a Lindemann glass capillary. The temperature was measured in a stream of cold nitrogen gas, at a distance of about 2 mm from the crystal. The unit-cell dimensions were determined from zero-layer Weissenberg and rotating-crystal exposures about [001], the long axis of the crystal: $a=18{\cdot}05\pm0{\cdot}02$, $b=10{\cdot}29\pm0{\cdot}01$, $c=3{\cdot}73\pm0{\cdot}01$ Å (λ Cu $K\alpha=1{\cdot}5418$ Å). Assuming four molecules in the unit cell, the calculated density (at 100°K) is 1·57 g.cm^{-3}. Equi-inclination Weissenberg photographs were made for *hk*0, *hk*1, and *hk*2 layers. The low-temperature equipment did not allow us to reach the necessary inclination angle to record the *hk*3 layer. The non-integrated reflexion intensities were estimated with a microdensitometer (Nonius I) and corrected by Lorentz, polarization and spot-shape factors. Because of the low linear absorption coefficient (μ Cu $K\alpha=10{\cdot}8$ cm^{-1}) and the small cross-section of the crystal ($0{\cdot}24\times0{\cdot}49$ mm^2), no absorption correction was applied. The structure factors from different layers were brought to absolute scale by comparison of F_o and F_c values. The total number of independent reflexions within the Cu $K\alpha$ sphere is 975, but only 586 were recorded, all with $|F_o|\neq0$, as follows:

*hk*0	195	(79·5%)
*hk*1	220	(86·9%)
*hk*2	171	(76·3%) .

Structure determination and refinement

The systematic absences observed on low-temperature Weissenberg photographs were

*h*00	if	$h=2n+1$
0*k*0	if	$k=2n+1$
00*l*	if	$l=2n+1$

Table 1. *Molecular orbital energies of π-electron systems (in β units, with α_C as the zero of energy)*

Geometry	R–N–N–N (I)	R–N, N, N (II)	R–N–N, N (III)	R–N, N, N (IV)
R = CH_3	9·64	10·22 ± 0·40	8·22 ± 0·40	9·62 ± 0·80
R = C_6H_5	18·10	18·68 ± 0·40	16·98 ± 0·40	18·38 ± 0·80
R = *p*-$O_2NC_6H_4$	24·94	25·52 ± 0·40	23·74 ± 0·40	25·14 ± 0·80

Table 2. *Final atomic parameters and their σ (fractions of cell edge), thermal isotropic factors* (Å^2), *and distances from the least-squares plane of the benzene ring* (Å)

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	B	d
C(1)	0·4659(8)	0·1729(13)	0·5377(49)	1·83	0·011
C(2)	0·4199(8)	0·0647(13)	0·5190(50)	1·95	−0·017
C(3)	0·3487(7)	0·0776(11)	0·6566(47)	1·65	0·010
C(4)	0·3247(7)	0·1949(12)	0·7886(46)	1·65	0·000
C(5)	0·3715(7)	0·3016(12)	0·7950(47)	1·58	−0·005
C(6)	0·4429(7)	0·2907(12)	0·6681(51)	1·83	0·000
N(1)	0·5397(6)	0·1614(10)	0·3893(42)	1·75	−0·042
N(2)	0·2507(6)	0·1959(10)	0·9153(40)	1·40	0·007
N(3)	0·2308(6)	0·3006(10)	1·0675(41)	1·40	0·123
N(4)	0·2068(7)	0·3878(11)	1·2085(45)	1·70	0·226
O(1)	·5607(5)	0·0565(10)	0·2688(37)	2·10	−0·043
O(2)	0·5801(5)	0·2601(9)	0·3767(37)	2·05	−0·126
H(1)	0·441	−0·016	0·424	1·8	
H(2)	0·316	0·002	0·647	1·8	
H(3)	0·349	0·392	0·907	1·8	
H(4)	0·478	0·377	0·679	1·8	

Table 3. *Observed and calculated structure factors*

Within each group the columns contain the values of h, F_o, $|F_c|$. Reflexions designated by an asterisk were corrected for extinction (see text).

K= 0 L= 1

2	15.0	17.2
4	21.2	24.6
6	52.6	57.0
8	40.2	39.4
10	47.7	45.7
14	4.7	4.5
16	4.8	4.3
18	6.7	8.1
20	3.3	3.3

K= 1 L= 0

2	18.9	21.4
4	14.3	14.6
5	32.8	34.8
6	35.1	37.0
7	12.1	12.6
8	48.3	47.5
9	3.6	3.6
11	14.6	13.3
12	10.8	9.1
13	24.7	25.3
14	10.3	10.3
15	9.9	9.5
16	4.4	4.4
17	3.5	4.0
18	3.3	4.8
19	5.7	6.9
21	4.1	4.4
23	3.2	4.1

K= 2 L= 0

0	85.9 *	81.6
1	67.6 *	65.0
2	14.4	15.5
3	9.8	8.9
4	26.6	27.6
5	36.5	39.5
6	26.2	25.5
7	35.3	34.2
8	16.0	16.3
9	16.3	14.3
10	15.8	12.8
11	13.9	13.2
12	4.9	4.0
13	2.7	1.3
14	16.9	16.7
15	11.7	11.0
16	4.5	4.5
17	7.7	9.0
18	4.7	5.1
20	7.2	8.3
22	5.4	6.4

K= 3 L= 0

1	13.9	14.3
2	4.3	4.2
3	14.6	12.3
4	8.1	6.5
6	30.0	28.9
7	4.0	1.1
8	14.9	14.2
10	10.3	9.5
11	15.8	15.5
12	5.2	4.1
13	23.8	23.1
14	31.3	33.1
15	7.1	6.9
16	10.9	10.4
17	4.8	6.4
20	10.2	11.8
21	3.1	4.4
22	2.7	2.5

K= 4 L= 0

0	9.1	8.0
1	27.7	29.8
2	8.5	8.4
3	10.9	10.8
4	13.6	14.7
5	46.6	47.3
6	32.0	30.7
7	11.1	11.0
8	4.8	3.0
9	13.6	13.3
10	5.0	3.9
12	21.6	20.7
13	16.2	14.9
14	4.3	3.8
15	32.0	33.7
16	11.5	11.9
19	6.8	8.3
20	6.6	7.3
21	3.4	3.6

K= 5 L= 0

1	8.4	8.5
2	5.9	5.7
3	24.3	23.1
4	21.0	21.2
5	8.4	8.2
6	5.7	4.0
7	11.2	10.3
8	5.5	6.8
9	13.7	13.2
10	11.0	10.6
11	3.1	3.2
13	18.7	17.5
15	4.6	5.6
17	5.4	5.0
18	9.9	9.5
19	6.0	6.5
21	2.6	5.8

K= 6 L= 0

0	4.5	3.9
2	2.7	2.9
4	27.0	26.2
5	6.9	5.6
6	15.7	13.4
7	4.2	3.8
8	15.4	15.8
9	6.7	7.3
10	10.5	10.5
11	3.2	3.6
12	17.0	15.8
13	12.1	13.0
14	26.7	27.5
15	14.6	14.5
17	7.0	8.3
19	5.8	6.3

K= L= 0

1	7.6	7.3
2	15.5	15.9
3	4.4	2.8
4	4.7	4.3
5	8.5	8.4
6	8.6	7.5
10	5.5	5.6
11	4.7	5.8
12	11.0	9.8
13	18.6	18.0
15	9.2	8.8
16	11.1	10.2
18	1.9	.7
19	10.4	12.3

K= 8 L= 0

0	35.4	38.0
1	18.1	18.7
3	19.6	20.3
5	9.7	10.6
6	6.6	6.0
7	3.2	3.9
8	10.2	4.1
9	12.1	11.3
10	22.7	25.3
11	7.8	7.0
12	2.9	4.3
13	11.3	10.4
14	7.1	8.1
16	7.5	7.5

K= 9 L= 0

1	7.9	8.0
2	24.4	24.4
3	5.8	7.5
4	7.8	7.3
5	5.1	3.9
8	9.4	10.1
10	9.5	10.1
11	7.8	6.7
14	2.9	3.0
15	7.1	6.4
16	4.3	5.2

K=10 L= 0

0	10.9	12.3
1	21.0	21.1
2	24.3	26.6
3	7.5	5.8
4	5.5	6.2
5	5.3	5.2
6	4.3	4.0
7	4.1	2.8
8	12.4	13.5
9	13.4	13.9
10	4.1	3.6
11	3.9	3.7
13	5.1	3.9
14	4.2	4.4
15	2.9	4.7

K=11 L= 0

1	3.9	4.2
2	6.2	6.0
4	11.6	13.2
5	2.6	2.6
7	9.4	8.4
8	7.2	9.0
9	5.6	5.9
10	6.4	6.5
11	3.8	4.9

K=12 L= 0

0	3.7	4.7
1	5.6	3.6
2	10.3	11.9
3	3.1	4.2
4	3.2	4.0
5	11.1	9.9
6	5.6	6.0
7	3.9	4.2
8	3.2	2.5

K=13 L= 0

1	4.8	6.2
2	5.1	5.1
3	4.3	4.6
4	2.8	2.7
5	.9	2.9

K= 0 L= 1

2	14.5	11.1
3	72.2 *	78.5
4	9.1	9.2
5	35.7 *	39.0
6	19.3	18.1
7	22.6	23.0
8	5.4	6.2
9	15.1	15.7
10	11.7	11.2
11	5.6	7.7
12	9.6	9.9
14	8.3	8.8
22	2.9	3.8

K= 1 L= 1

0	14.8	18.5
1	50.4 *	55.1
2	79.0 *	86.5
3	66.7 *	62.5
4	29.2	32.5
5	19.0	19.3
6	6.5	6.6
7	16.0	14.0
8	40.8	42.2
9	17.9	17.3
10	15.8	15.0
11	22.3	21.6
12	11.9	11.8
14	4.6	4.1
15	11.6	11.4
16	12.9	12.4
17	9.9	10.3
18	4.4	4.8
19	3.4	2.7
21	3.7	4.5
22	2.9	3.6

K= 2 L= 1

0	8.9	11.9
1	23.2	23.8
2	68.5 *	62.7
3	9.2	7.5
4	15.1	16.1
5	9.3	9.5
6	18.8	17.4
7	4.6	5.5
8	7.2	6.5
9	12.5	11.8
10	24.6	24.1
11	14.5	14.2
12	12.6	11.4
13	7.3	6.8
15	15.9	16.0
16	16.1	15.5
17	17.6	19.8
18	5.0	4.9
21	5.0	5.7
22	5.0	7.6

K= 3 L= 1

0	17.5	18.6
1	18.5	20.2
2	25.9	26.5
3	22.8	23.5
4	8.7	8.8
5	4.4	3.4
6	4.6	3.2
7	20.5	19.2
8	22.7	22.3
9	16.1	16.1
10	13.9	11.7
11	13.0	12.7
12	17.8	17.3
13	19.7	19.4
14	10.0	9.0
15	5.4	5.1
16	8.0	8.2
17	10.9	11.4
18	4.9	4.7
20	5.2	5.6
21	7.5	4.5
22	2.9	4.7

K= 4 L= 1

0	3.5	6.4
1	14.2	13.3
2	15.4	13.4
3	12.0	12.3
4	20.6	19.2
5	3.4	2.5
6	14.2	15.5
7	14.0	13.5
8	14.6	13.0
9	6.7	5.8
10	8.6	7.3
11	16.7	16.4
12	18.1	18.1
13	8.5	8.7
14	9.6	9.5
15	6.6	6.8
16	11.3	10.8
17	12.0	11.6
18	3.3	3.5
19	6.0	7.6
20	4.4	4.6
21	5.8	8.3

K= 5 L= 1

0	13.2	12.1
1	16.3	15.6
2	13.5	12.0
3	21.7	21.2
4	25.5	26.9
5	11.0	9.7
6	23.2	22.5
7	11.7	10.7
8	6.8	6.1
9	15.5	14.8
10	9.6	7.5
11	15.3	14.0
12	26.1	25.6
13	21.2	20.3
14	16.3	14.2
15	6.4	6.8
16	5.0	4.1
17	7.9	8.2
18	6.8	6.3
19	5.0	4.1
21	2.8	7.0

K= 6 L= 1

0	10.2	9.3
1	6.3	6.7
2	15.3	13.7
3	8.7	7.5
4	8.6	7.7
5	10.4	10.1
6	7.8	6.4
7	11.5	9.4
8	11.8	11.0
11	9.4	7.7
12	19.5	20.0
13	3.8	3.2
14	13.5	13.7
15	11.5	10.5
16	7.5	7.7
17	8.1	8.9
18	4.7	5.8
19	6.9	7.8
20	4.0	3.9

K= 7 L= 1

0	4.9	3.9
1	15.9	15.9
2	17.7	16.9
3	7.1	6.5
4	9.7	9.5
5	11.7	10.0
6	12.4	11.3
7	14.5	13.3
8	10.2	9.7
9	4.7	3.2
10	11.3	13.3
11	10.0	9.1
12	14.3	14.3
13	8.1	7.3
14	6.0	5.4
15	11.7	12.1
16	6.0	6.8
17	5.8	6.0

K= 8 L= 1

0	13.4	13.6
1	9.5	8.4
2	12.7	11.8
3	12.2	11.0
4	12.2	10.9
5	5.3	5.4
6	4.7	5.1
7	9.4	9.5
8	6.6	6.9
12	6.1	7.1
13	5.8	6.1
14	10.4	10.1
15	7.5	7.4
16	6.6	6.2
17	3.6	3.5

K= 9 L= 1

0	11.6	10.3
1	22.7	21.1
2	20.5	20.2
3	6.6	6.4
4	14.3	13.4
5	9.9	9.5
6	16.9	16.4
7	10.4	10.4
8	6.4	7.7
9	8.0	9.2
11	5.7	6.3
12	8.7	8.9
14	6.9	7.8
15	5.6	7.2
16	2.8	4.4

K=10 L= 1

1	19.1	19.0
3	8.6	8.1
4	4.4	4.1
6	10.0	10.2
7	9.1	9.5
8	4.0	4.4
9	5.7	6.3
10	5.4	6.8
11	6.0	6.2
12	6.1	7.2

K=11 L= 1

0	22.0	22.5
1	5.2	6.2
2	4.0	3.5
3	4.0	2.8
4	4.5	5.5
5	6.2	6.9
6	6.0	5.6
7	3.5	3.6
8	3.3	3.6
9	4.3	5.0
10	5.7	6.6
11	2.0	2.4
12	2.2	4.0

K=12 L= 1

0	5.7	7.3
1	6.9	6.5
2	3.2	4.0
3	3.1	2.7
4	7.6	8.5
6	4.0	5.1
7	7.1	7.1
8	5.9	8.1

K=13 L= 1

0	2.2	4.9
1	1.6	4.4
2	1.5	4.3

K= 0 L= 2

3	32.9 *	34.4
4	22.3	21.3
5	29.0	29.5
6	20.3	17.2
7	21.6	20.0
8	19.4	18.5
9	8.7	8.2
11	4.7	3.0
12	11.6	11.4
13	12.1	12.3
14	10.1	10.7
15	11.4	14.1
16	11.8	12.2
17	8.9	10.4
18	10.7	11.4

K= 1 L= 2

0	8.3	9.9
1	14.4	22.3
2	9.7	8.5
3	23.0	21.3
4	24.1	23.0
5	24.8	24.0
6	17.1	15.0
7	14.1	15.4
8	8.7	6.5
9	12.0	12.0
12	7.0	7.5
13	10.1	10.7
14	5.0	5.5
16	9.6	10.1
17	6.4	5.7
18	9.1	10.2
19	8.1	9.9

K= 2 L= 2

0	8.8	8.2
1	8.2	5.4
2	18.8	17.3
3	22.8	24.6
4	22.2	21.4
5	27.0	26.0
6	14.3	14.1
7	7.9	6.6
8	8.7	7.1
9	11.3	12.0
10	16.6	16.6
11	6.9	6.0
12	7.1	5.9
13	5.0	4.4
15	7.0	8.7
17	6.3	5.1
18	7.5	7.5
19	8.4	10.4
20	5.7	7.2

K= 3 L= 2

0	27.1	26.8
1	11.1	11.0
2	27.2	27.3
3	13.2	11.9
4	23.2	22.4
5	11.0	10.2
6	17.4	18.3
7	5.3	3.6
8	13.4	11.7
9	12.8	11.8
10	12.7	12.8
11	11.8	11.7
12	9.7	8.6
13	15.3	15.2
14	10.7	10.0
17	4.3	5.3
18	4.7	6.5
19	8.4	11.4
20	3.7	5.3

K= 4 L= 2

1	19.8	19.1
2	17.1	16.6
3	13.6	12.1
4	5.9	5.6
5	6.1	5.1
6	5.5	4.1
7	9.9	9.8
9	12.2	12.3
10	21.4	21.5
11	26.6	27.0
14	3.4	4.7
15	4.6	4.9
16	5.4	6.7
17	4.0	5.2
19	5.2	5.9

K= 5 L= 2

0	21.4	18.0
1	8.5	7.6
2	10.7	12.7
3	12.9	11.8
4	16.3	17.2
5	8.9	9.3
6	7.5	6.6
7	9.3	8.9
8	6.1	5.7
9	17.3	17.6
10	19.8	21.0
11	9.7	9.1
12	11.5	11.6
13	4.8	5.7
14	6.6	6.1
15	6.3	6.3
18	6.2	6.8
19	5.2	7.2

K= 6 L= 2

0	10.2	10.6
1	12.3	11.9
3	5.9	6.3
4	12.1	11.8
5	9.4	7.1
6	8.6	7.2
7	11.7	10.7
9	16.3	16.5
10	13.4	12.2
11	14.4	14.8
12	8.7	8.2
14	4.3	4.7
15	7.0	7.7
17	6.6	9.1

K= 7 L= 2

2	10.7	9.0
3	17.8	16.0
4	20.4	21.1
5	11.5	11.1
6	8.7	8.3
7	8.7	8.9
8	7.1	6.2
9	4.9	2.3
11	9.8	9.5
13	6.0	6.8
14	3.9	5.4
15	5.4	5.2
16	6.0	7.9
17	5.6	9.3

K= 8 L= 2

2	7.2	6.4
3	5.0	3.5
4	20.1	20.4
5	7.1	6.9
6	13.7	13.2
7	6.9	7.6
8	5.9	6.5
9	5.7	5.5
10	6.3	6.7
11	3.0	2.8
12	2.8	2.7
13	5.1	6.5
14	4.5	3.8
15	4.5	4.2

K= 9 L= 2

1	8.7	7.7
2	9.1	9.7
3	10.0	10.3
4	8.6	8.8
5	11.4	9.5
8	3.0	1.9
12	3.2	3.5
13	2.7	3.7

K=10 L= 2

0	6.2	5.2
1	7.5	5.0
2	8.9	8.7
3	7.5	6.7
4	12.1	11.7
6	6.8	8.1
7	3.7	3.9
8	6.1	6.9
9	4.6	4.6
11	3.4	3.2

K=11 L= 2

2	8.9	9.0
3	10.4	11.2
4	7.1	7.8
5	4.4	5.1
6	4.4	5.6
7	4.9	5.3

K=12 L= 2

0	4.4	7.1
1	2.9	3.9

confirming the space group $P2_12_12_1$ previously found (Mugnoli & Mariani, 1964). The refinement was carried out on structure factors observed at 100°K, taking as a starting point the atomic coordinates as obtained in the previous work at room temperature. A first $\varrho(x,y)$ synthesis was calculated and from the heights of the peaks on the projection a preliminary set of isotropic thermal factors was deduced (Nardelli & Fava, 1960). The next F_c set was obtained including the four hydrogen atoms placed at 1·08 Å from the bonded carbon along the straight line through the projections of the opposed carbons on the average plane for the benzene ring. The following values resulted for the R index (observed reflexions only): $R(hk0)=11{\cdot}7\%$, $R(hk1)=13{\cdot}3\%$, $R(hk2)=15{\cdot}3\%$. The position refinement for all but hydrogen atoms proceeded with a few differential synthesis cycles (F_c calculated including hydrogen contributions as before). The general agreement was good, except for nine low-index reflexions, with $F_c \gg F_o$. An empirical extinction correction was then applied (Pinnock, Taylor & Lipson, 1956). The least-squares line equation through these nine points was

$$I_c/I_o = 1{\cdot}0 + 1{\cdot}5 \,.\, 10^{-4} I_c \,.$$

The corrected values appear in Table 3 with an asterisk. To improve the thermal factors, $\varrho(x_i, y_i, z_i)$ was calculated for each atom i, including the observed factors for $hk0$, $hk1$, $hk2$ layers and calculated ones for $hk3$ and $hk4$ layers. The new set of B_i factors as a function of $\varrho(x_i, y_i, z_i)$ was obtained from known tables (Nardelli & Fava, 1960). A mean value $B_H = 1{\cdot}8$ Å^2 was assigned to the four hydrogen atoms.

Three more differential synthesis cycles were performed, then a difference synthesis $\varrho(x, y)$ was computed, with the contributions of C, N, and O atoms subtracted from the observed factors. This projection allowed us to obtain x and y coordinates for the hydrogen atoms. The average plane for the benzene ring was then determined by the method of Schomaker, Waser, Marsh & Bergman (1959). For each carbon atom the distance from this plane (see Table 2) is less than the corresponding $\sigma_\perp$ (standard deviation for the position along the direction perpendicular to the plane mean 0·017 Å). The z coordinates for the hydrogen atoms were assigned assuming coplanarity with the carbon atoms. The results of the last structure factor calculation are collected in Table 3. Final values for the R index (observed reflexions only) are: $R(hk0)=8{\cdot}01\%$, $R(hk1)=8{\cdot}41\%$, $R(hk2)=10{\cdot}03\%$. The overall R index is 8·70%.

Fig. 1 shows the final $\varrho(x, y)$ projection; the hydrogen atom peaks come from the difference synthesis. The positional and thermal parameters are shown in Table 2. Values of σ's for the coordinates were calculated according to Cruickshank (1949). Bond distances and angles and their σ's (Cruickshank & Robertson, 1953) are collected in Figs. 2 and 3.

The equation for the least-squares plane of the benzene ring is:

$$0{\cdot}3152X - 0{\cdot}2669Y + 0{\cdot}9107Z - 3{\cdot}991 = 0$$

where X, Y, Z are coordinates in Å. The angle between the N_3 chain and the benzene ring is about 5·3°. The equation for the least-squares plane through all heavy atoms except N(3) and N(4) is

$$0{\cdot}3316X - 0{\cdot}2534Y + 0{\cdot}9088Z - 4{\cdot}115 = 0 \,.$$

For these atoms the maximum distance from the plane is 0·046 Å. No sensible rotation of the nitro group around the C(1)–N(1) axis with respect to the ring plane was found. Fig. 4 shows the molecular packing along [010] and [001], and the intermolecular contacts shorter than 3·70 Å. Owing to the uncertainty in coordinate values no distances from hydrogen atoms are shown; in no case, however, even considering the H atoms, are these distances less than the sum of van der Waals radii. The spacing between the planes of the nearest parallel benzene rings is 3·40 Å.

Discussion

The benzene ring is not far from a regular hexagon, with average C–C distance 1·382 Å. No quinoid structure appears here, in contrast to what might have been suggested by theoretical considerations. The electronic structure of the molecule has been investigated by the Hückel molecular orbital (HMO) method, in the approximation usually known as ω-technique, with $\omega = 1{\cdot}25$ (Streitwieser, 1962), taking care of variation of β with distances as in a previous calculation on phenyl azide (Favini, 1961). The bond orders – bond distances relationships given by Coulson (Coulson, 1939; Moser, 1953) for C–C bonds and by Gordy (Gordy, 1947; Favini, 1961) for other bonds have been used throughout. The final results of the HMO calculations are: C(1)–C(2) 1·43; C(2)–C(3) 1·37; C(3)–C(4) 1·43; C(1)–N(1) 1·37; N(1)–O(1) 1·28; C(4)–N(2) 1·35; N(2)–N(3) 1·34; N(3)–N(4) 1·17 Å. The calculated shortening of the C(2)–C(3) and C(5)–C(6) bonds, and the lengthening of the other bonds in the ring, as compared with the benzene value, is not observed in the crystal structure. The agreement between theoretical and experimental values for distances outside the ring is also rather poor. It seems that the standard deviations on the bond distances (mean, 0·018 Å) are not sufficient to explain this as a pure consequence of observational errors. Three explanations could be suggested to justify the discrepancy: poor approximation of the calculated bond orders, naivety of the bond order – bond length relationships, distortion of molecules on packing.

The C(1)–N(1) distance is slightly shorter than values found for other nitro compounds (nitrobenzene 1·486 Å, Trotter, 1959*a*; *p*-dinitrobenzene 1·48 Å, Abrahams, 1950; *m*-dinitrobenzene 1·47 Å, Trotter, 1961) and is comparable to the value found for *p*-nitroaniline (1·460 Å, Trueblood, Goldish & Donohue, 1961), for α-*p*-nitrophenol (1·442 Å, Coppens & Schmidt, 1965) and for 9,10-dinitroanthracene (1·45 Å, Trotter, 1959*b*). Also the N–O bond distances found for this last struct-

ure (1·24 Å), for *p*-nitroaniline (1·247 Å), for α-*p*-nitrophenol (mean, 1·234 Å) and for *N*,*N*-dimethyl-*p*-nitroaniline (1·250 Å, Mak & Trotter, 1965) are in agreement with our mean value. The O–N–O angle is slightly smaller than in some of the previous compounds, but close to the corresponding one in 9,10-dinitroanthracene (120°), in α-*p*-nitrophenol (122·0°) and in *N*,*N*-dimethyl-*p*-nitroaniline (121·4°). This last compound shows a remarkable quinoid structure that is not evident in *p*-nitrophenyl azide nor in α-*p*-nitrophenol.

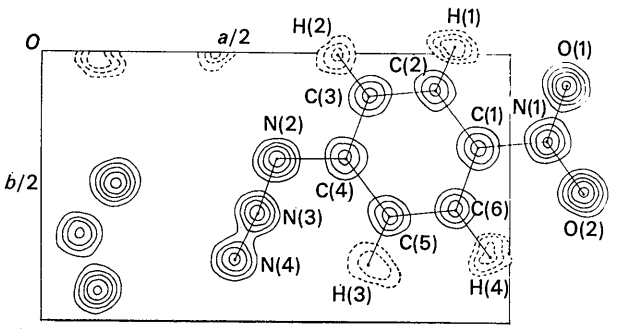

Fig. 1. The electron density projected onto (001). Heavy atoms: continuous contours, at intervals of 2 e.Å^{-2} beginning with 4 e.Å^{-2}. Hydrogen atoms (from difference projection): dashed contours, at intervals of 0·2 e.Å^{-2} beginning with 0·5 e.Å^{-2}.

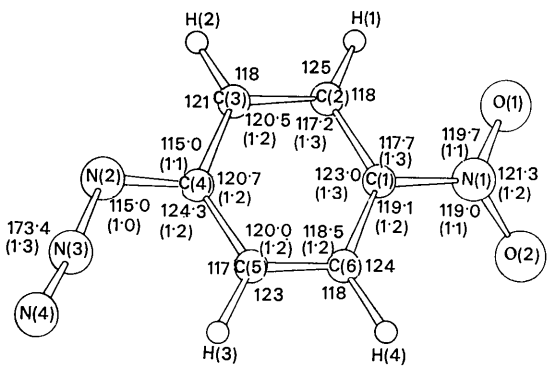

Fig. 2. Bond distances (in brackets, $\sigma \cdot 10^3$) in Å.

The C(4)–N(2) distance is appreciably shorter than the corresponding one in methyl azide (1·47 Å, Livingston & Rao, 1960); this is due to the bond order effect (our calculated value $n = 1{\cdot}55$ corresponds to a still shorter distance) and to the lower value of carbon radius for sp^2 than for sp^3 hybridization (Coulson, 1959). The C(4)–N(2)–N(3) angle is in the expected range. The N(3)–N(4) bond is considerably shorter than the N(2)–N(3) bond, qualitatively in agreement with theoretical predictions and consistent with previous results for cyanuric triazide, methyl azide and hydrogen azide. A less marked asymmetry of the same kind has been observed by Palenik (1964) for the coordinated azido group in azidopentamminecobalt(III) azide. In our compound, the N(2)–N(3)–N(4) angle is significantly smaller than 180°. The strongest bending in an azide chain was found in the adduct of picryl azide with bis-8-hydroxyquinolinatocopper(II) (Bailey, Merer & White, 1965), the angle N–N–N being 168·3° (e.s.d. 1·8°).

All calculations were performed on an IBM 1620 20K computer using programs written in FORTRAN by one of us (C.M.). Atomic scattering factors were calculated by means of the analytical expressions due to Forsyth & Wells (1959).

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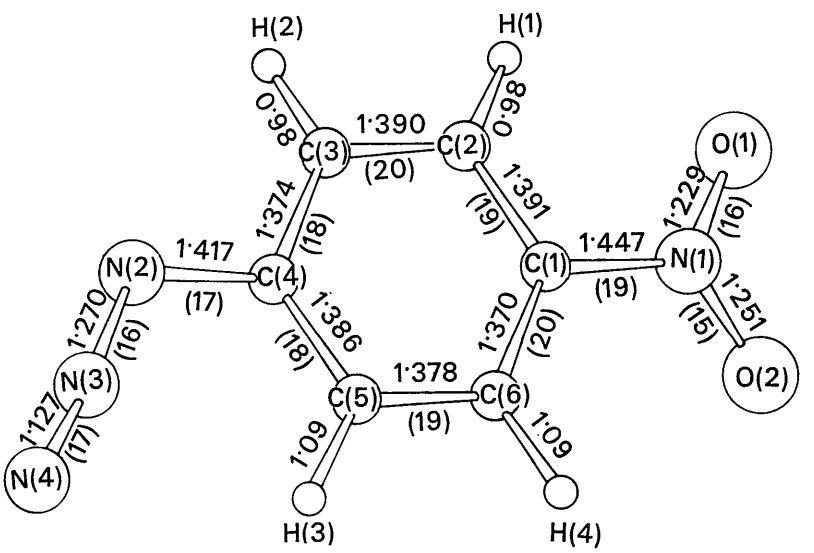

Fig. 3. Bond angles (in brackets, σ) in degrees.

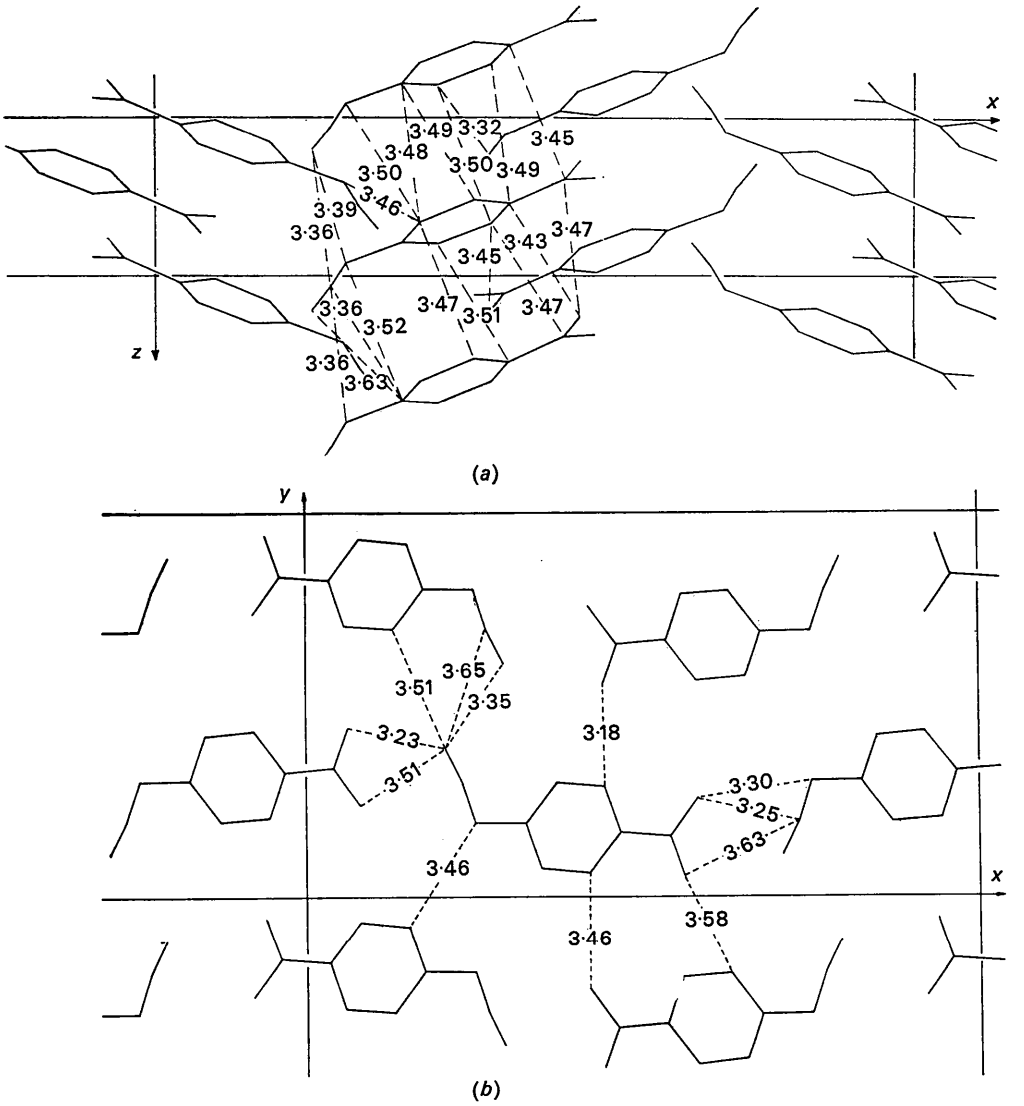

Fig. 4. Molecular packing viewed (*a*) along the [010] axis, (*b*) along the [001] axis. Only intermolecular distances shorter than 3·70 Å are shown.

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