Acta Cryst. (1956). **9**, 787

On the Structure of 4-Nitropyridine-*N*-Oxide*

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(*Received 27 October 1955 and in revised form 16 January 1956*)

4-Nitropyridine-*N*-oxide has the space group $Pnma$–D_{2h}^{16}, with 4 molecules per unit cell, arranged paired in mirror planes. The problem is thus reduced to two positional parameters per atom, which were refined by simultaneous differential syntheses and a least-squares procedure, using zero- and first-layer data to separate the mirror planes in the unit cell. A percentage discrepancy of less than 11% was obtained for all data, with a standard deviation $\sigma_{xz} \approx 0.009$ Å in the parameters. The bond lengths proved to be symmetrically equal with respect to the axis of the molecule. A somewhat more pronounced quinoidal character of the ring was found than had been expected. A discourse upon refinement criteria and 'optimalization' is introduced. It is concluded that (possibly only in this particular case) differential syntheses refine with faster convergence than least-squares methods where $\omega = 1/F_o$.

Preamble

In the past decade organic chemists have explored the properties of heterocyclic *N*-oxides with a view to the establishment of substitution syntheses. Pyridine itself, for example, is not easily accessible to classical substitution reagents, and whenever substituted pyridines were so obtained, the yield was usually poor and the effort considerable. Bobranski, Kochanska & Kowalewska (1938) published on substitution reactions for pyridine, involving *N*-oxides as intermediates, and after a temporary standstill two very active groups (Ochiai (1953) in Japan, and den Hertog in the Netherlands (Hertog & Combé, 1951; Hertog, Kolder & Combé, 1951; Hertog & Overhoff, 1950)) poured out one communication after the other describing substitution syntheses via the *N*-oxides for nitrogen-containing heterocyclic compounds. The yields now obtained were generally excellent. Interest in the *N*-oxides led to the investigation of their properties also by physico-chemical methods, i.e. spectroscopy and electrometric analysis, and lately publications have appeared carrying this interest into the realm of quantum mechanics (Jaffé & Doak, 1955).

It seemed to us that an accurate set of bond data should be made available; we were also interested in the different types of C–N and N–O bonds within the same molecule of 4-nitropyridine-*N*-oxide.

Another reason was furnished by the results of studies upon nitroaniline (Abrahams & Robertson, 1948; Abrahams, 1952). There, intramolecular resonance interaction was presumed, since two vicinary molecules are separated by a very short distance and hydrogen bridges had to be discounted on various evidence. Interaction between π electrons of the ring of one molecule with the nitro group of the neighbouring one would appear to produce a 'self-complex'. We could reasonably expect a similar situation in the 4-nitropyridine-*N*-oxide.

It was therefore decided to obtain the best possible bond-length and bond-angle data, utilizing X-ray spectra taken at 25° C. first, and to extend the investigation, if promising, to the low-temperature range later, and possibly to other compounds of the pyridine-*N*-oxide series.

Experimental part

4-Nitropyridine-*N*-oxide was obtained from pyridine by oxidation with peracetic acid and subsequent nitration. The crude orange product recovered from the reaction mixture by ether extraction was then recrystallized, first with ligroin, and finally with a mixture of acetone and ligroin. The yellow crystals

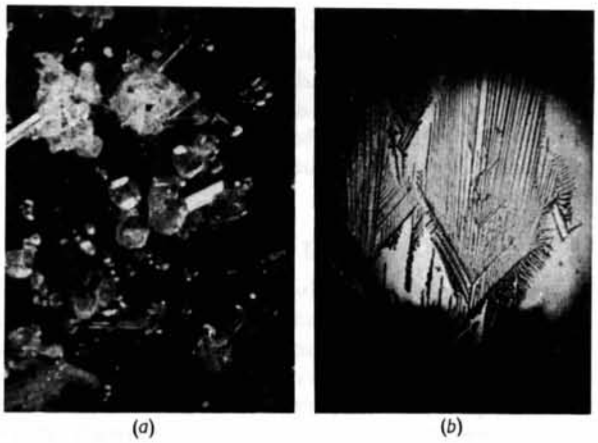

Fig. 1. (*a*) Clusters of needles and polyhedra. All three types of habit can be seen. The two types of needles (|| *a* and || *c* axis) can only be distinguished through examination with an optical goniometer or X-rays.

(*b*) Dendrites of 4-nitropyridine-*N*-oxide, showing the fish-tail development along diagonal directions.

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* Contribution No. 2048 from the Gates and Crellin Laboratories, California Institute of Technology.

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so procured show three types of habit, readily recognizable under the microscope (Fig. 1(*a*)): (*a*) needles || *a* axis; (*b*) needles || *c* axis; (*c*) almost globular polyhedra.

Very well developed crystal faces permitted a full morphological study with an optical goniometer, and orthorhombic symmetry (bipyramidal) could be established offhand. The density, by flotation, was $d_f = 1{\cdot}52$ g.cm.$^{-3}$.

A suitable crystal of habit (*c*) was selected with optimal diameter of 0·18 mm. ($\Sigma_i p_i.(\mu/\varrho)_i = 7{\cdot}25$). It was treated with liquid air to minimize extinction effects in the observable intensities.

Zero-, first- and second-layer Weissenberg data were then taken at room temperature about all three axes, using the multiple-film technique and copper *K* radiation.

The conditions for reflexion were:

(hkl) and ($h0l$): no condition; ($0kl$): $k+l = 2n$; ($hk0$): $h = 2n$;
($h00$), ($0k0$) and ($00l$): $h, k, l = 2n$.

The space group was assumed to be $Pnma\text{–}D_{2h}^{16}$, the unit cell containing four molecules.

This establishes the very favourable situation of two mirror planes $\frac{1}{2}b$ apart, each plane containing two molecules flat within it; positions:

$(x, \frac{1}{4}, z)$ and $(\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$ for one mirror plane,
$(\bar{x}, \frac{3}{4}, \bar{z})$ and $(\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z)$ for the second.

The cell dimensions are:

$$a = 12{\cdot}53\pm0{\cdot}01,\ b = 6{\cdot}04\pm0{\cdot}01,\ c = 7{\cdot}93\pm0{\cdot}01\ \text{Å};$$
$$V = 600\pm2\ \text{Å}^3;\ d_X = 1{\cdot}55\ \text{g.cm.}^{-3}.$$

The systematic absences in the reciprocal lattice would, of course, equally permit the choice of the acentric space group $Pn2_1a\text{–}C_{2v}^{9}$. However, the strong and regularly occurring pinakoidal development of faces in all of the many crystal batches that we obtained, combined with the evidence provided by the presence of habits (*a*) and (*b*), made us decide to base a trial model on the assumption of the centric case. The convergence of refinement to the fairly low value of percentage discrepancy obtained finally, bore out this assumption.

The trial structure

Because of the very nearly equal scattering weight of the carbons, nitrogens and oxygens, and the general hexagonal pattern of the molecule, no great aid in the determination of the structure was expected from vector maps, and we therefore did not utilize any. The diagonal zone [$10\bar{2}$] showed up strongly in the reciprocal-lattice pattern and suggested a fish-tail arrangement of the molecules within the mirror planes. The compound will also form beautiful dendrites (Fig. 1(*b*)), oriented along the diagonals, and Bragg–Lipson charts equally pointed to the fish-tail layout. In the end only two main possibilities appeared to exist, essentially similar, but with the 'front' and 'tail' of the molecule inverted. Only one of these trial structures, however, refined properly, and after eleven refinement operations yielded the final parameters (Fig. 2).

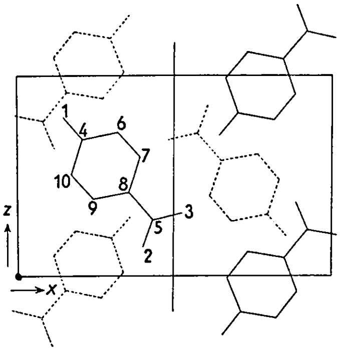

Fig. 2. Arrangement of the four molecules in the unit cell, seen in ($h0l$) projection. Broken lines represent molecules in lower layer.

Refinement

The planar arrangement and the space group immediately suggested the use of generalized transforms, utilizing zero- and first-layer data, i.e. ($h0l$) and (hll). The intensities of 202 observable spots were estimated very carefully, corrected, and checked with Weissenberg data from photos taken about the *a* and *c* axes. The layers $y = \frac{1}{4}$ and $y = \frac{3}{4}$ were then separated by a generalized Fourier method, a variant of the Booth differential synthesis, which permitted the assumption of full resolution of density peaks. Refinement was

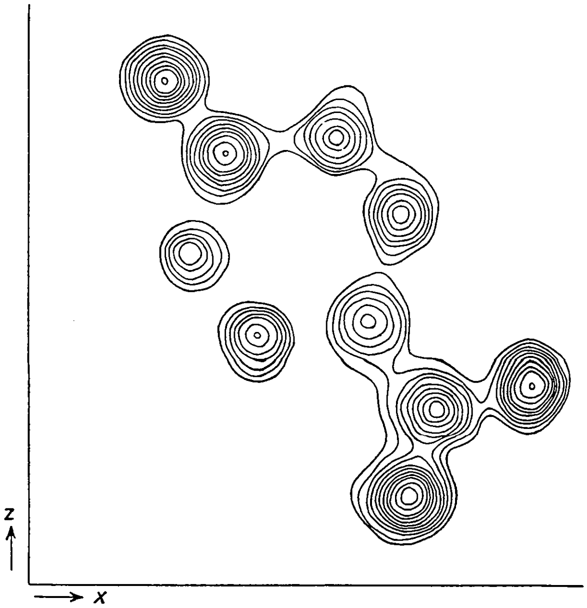

Fig. 3. Generalized Fourier projection of the asymmetric unit. Projection axis || *b*. Contour levels on arbitrary scale.

carried out entirely by numerical analysis and the density map (Fig. 3) was drawn only for illustration after all phases had been obtained from generalized differential syntheses.

All arithmetical operations were carried out on an I.B.M. 604 digital computer and the array of auxiliary punched-card equipment that goes with it. In the later stages of refinement the non-observed planes were also computed (61 such amplitudes), and the hydrogen contribution was included.

Upon comparison of the formulae for both methods, it was found that no great loss in time would be incurred if refinement cycles were to be calculated according to the differential method of Booth (1946) and simultaneously according to the method of least-squares (Hughes, 1941); the transcendental functions to be computed are the same in both cases. The weight was chosen to be $1/F_o$ in all cases bar one, for the least-squares refinement. The formula used then is

$$\Delta x . \Sigma_H (1/F_o) . (\delta F/\delta x)^2 = \Sigma_H (\Delta F/F_o) . (\delta F/\delta x) .$$

In the case of the differential synthesis the formula is

$$\Delta x . (\delta^2 \varrho/\delta x^2) = -(\delta \varrho/\delta x) ,$$

where the quantity Δx has to be computed for both the F_o (with F_c phases) and the F_c set, to obtain proper back-shift correction (termination-of-series error). In the later stages of refinement, the curvatures do not alter very much, and it is permissible to obtain shifts in the differential method by effectively utilizing a differential difference synthesis, i.e. the right hand term becomes $-(\delta \Delta \varrho/\delta x)$.

The rate of attrition of the percentage discrepancy is set out in Fig. 4. It can be seen that the differential method in all cases converges much faster than the least-squares one with $\omega = 1/F_o$. In one case ω was chosen to be 1 rather than $1/F_o$ and in this particular instance convergence was nearly as good as in the differential method. It was first thought that the difference in refinement criteria would be responsible for this slower convergence of the least-squares method, for where the differential synthesis will move the input position toward the density core of the transform, the least-squares method will equalize F_o and F_c, and therefore tend to compensate for the absence of hydrogens. However, even after the hydrogens were put in, no better convergence could be obtained. It is very likely that the weighting $1/F_o$ was unsuitable and that such weighting would very much depend on the structure. We do not think that an offhand recipe can be given for the type of ω to be chosen in a particular problem.

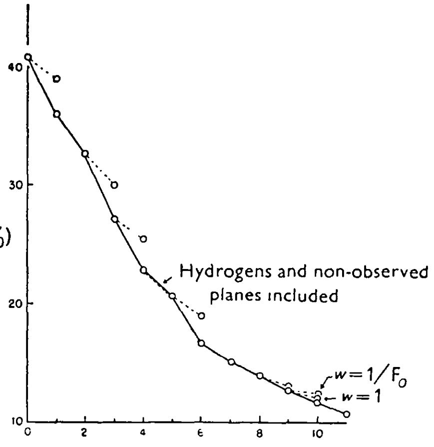

Fig. 4. Rate of attrition graph. Broken lines: least-squares for $w = 1/F_o$; full lines: differential syntheses.

The statistics of the refinement are (per cycle):

4 hours machine time on various I.B.M. machines for the differential synthesis shifts of ten atoms (40 shifts);
1 additional hour for the least-squares computation (20 shifts);
3 hours machine time for calculation of structure factors (geometrical part) for ten atoms and 263 reflexions;
1 hour machine time for optimalization of temperature factors and printing of data lists.

It must be noted that the contribution of the hydrogen atoms was computed once, and this contribution from then on was treated as a constant.

The non-observable reflexions were treated in the following way: they were assigned an amplitude equal to half the threshold observable value in this $\sin^2 \theta$ range. Where the computed amplitude proved to be higher than this assigned amplitude, the difference ΔF was maintained in subsequent refinement. Where it was smaller, the assigned value was replaced by F_c, ΔF thus being zero.

Optimalization

For some time in the past the author has used an 'optimalization' procedure in refinement of structures, based upon the expression

$$R_2 = \Sigma_H (n . F_o - F_c)^2 / n^2 . \Sigma_H F_o^2 ,$$

where n is the scale factor and F_c includes the Debye exponential.

It can be shown very easily, either by differentiation or by algebra analysis, that for a given Debye exponential factor (B), the lowest R_2 value will be obtained for

$$n_\Omega = \Sigma_H F_c^2 / \Sigma_H F_o . F_c ,$$

where F_o represents the observed value on an arbitrary scale.

Upon reintroducing n_Ω into the formula of R_2, one then finds the optimal R_2 value for a given temperature movement:

$$R_{2\Omega} = 1 - (\Sigma_H F_o . F_c)^2 / (\Sigma_H F_o^2 . \Sigma_H F_c^2) = 1 - k_\Omega .$$

The value k_Ω is called the 'goodness-of-fit'. The higher k_Ω, the lower the R_2 value and the better the agreement between observed and computed amplitudes.

The function $R_1 = \Sigma_H \Delta F / \Sigma_H F_o$, although arithmetically less accessible, has the merit of tradition, and we have compromised with this tradition by adopting the r.m.s. percentage discrepancy

$$R_{21} = \sqrt{R_2} \text{ in percent}\,.$$

It was found in practice upon numerous examples that there is practically no difference between the numerical values of optimal R_1 and optimal R_{21} percentages, and the two are therefore comparable directly.

However, we felt no doubt that the use of R_2 and R_{21}, respectively, was much more desirable in that it permits the computation of optimal scaling on a direct basis. The function $[R_{21} = f(n)]_{B=\text{constant}}$ has, moreover, only one extreme value; the equivalent expression utilizing R_1 theoretically need not.

Expressions are derivable for the optimalization of R_2 with respect to heat movement of the atoms, and it is proposed to treat this more involved subject elsewhere. It is, however, quite easy to plot R_Ω, or rather k_Ω, as a function of B, when a digital computer is available, since the three sums involved in the formulae can readily be calculated for a set of sequential B-values (in the ideally isotropic case). The maximum of $k_\Omega = f(B)$ will then furnish the penoptimal set:

$$n_{\Omega\Omega},\ R_{21\Omega\Omega}, \text{ and } B_\Omega.$$

This was done in exactly the described way on the I.B.M. 604 machine after each refinement cycle. A typical graph is represented by Fig. 5.

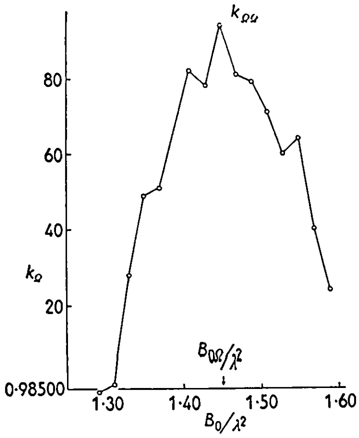

Fig. 5. Typical optimalization graph. The discontinuities in the graph are mostly the result of rounding-off errors. The graph should therefore mentally be replaced by the smoothest fitting continuous curve.

Heat movement

The case of 4-nitro-pyridine-*N*-oxide can be dealt with in a fairly simple manner because of the layer arrangement of the molecules, where the molecules have to be completely flat by dint of symmetry. A more or less reliable rule of thumb would state that there must be at least twenty equations per parameter in the structure-factor calculations, and the number of data in our case was such that we would not have been justified to assign individual and asymmetric temperature factors to each atom. In point of fact such a procedure would have ignored the probability of different charges (formal) on different component atoms. But we felt, on the other hand, that we were safe in assuming a fairly isotropic movement of scattering matter within the molecular plane, and a different heat movement perpendicular to that plane. In short, we introduced from the theory of elasticity an oblate spheroid in our picture of the crystal unit cell such that its surface would represent the boundary of temperature movement vectors of the scattering mass. The plane of the molecule would then intersect this ellipsoid in a circle; all other planes, not parallel to this plane, in an ellipse. This case can be treated simply by analytical geometry for the direct Bravais lattice, and has been applied several times by various authors to the reciprocal lattice (where it is represented, in general, by a more elegant formula). For reasons connected with the available sub-routines for our computer, we chose the expression for the direct cell, where

$$F_c = F_g \exp\left(-B . \sin^2\theta/\lambda^2\right);$$

B = Debye factor, F_g = geometrical part of the amplitude.

It can be shown then, that in the case of the elastic oblate spheroid B must be replaced by a function R:

$$R = B_0 B_1 / \sqrt{\{B_0^2 . \cos^2\varphi + B_1^2 . \sin^2\varphi\}}\,,$$

where B_0 would be the Debye vector within the molecular plane, and B_1 the vector perpendicular to that plane; φ represents the angle between the normals of the molecular plane and the plane (hkl).

It can be seen that for the zone $(h1l)$ simplifications are possible when B_0 and B_1 are not very greatly different, and upon certain conditions of cell dimensions. It was found in our present case that only two planes from the $(h1l)$ set had a fairly small value for φ. For all other planes φ was large enough to permit the assumption of $R \approx B_1$ (to within 1%). Fortunately the two planes with small φ also have a very small $\sin^2\theta$ value, and are therefore insensitive to large variations in the Debye factor. We could therefore treat the $(h1l)$ set of planes as though they would all have a Debye factor B_1; the approximation in our case was very close and the error so introduced proved to be very much smaller than those introduced by subjectivity of intensity estimation, rounding-off in the arithmetical operations, etc.

In the final analysis the ensuing values were found:

$$(h0l)\colon\ B_0 = 3{\cdot}45 \pm 0{\cdot}03\ \text{Å}^2\,,$$
$$(h1l)\colon\ B_1 = 4{\cdot}40 \pm 0{\cdot}04\ \text{Å}^2\,.$$

It was tempting to convert the B_1 value into a mean displacement of the molecule perpendicular to its plane; how significant the resulting figure is, is somewhat in doubt, but we represent it here for what it is worth:

$$B_1 \approx 8\pi^2 . \langle u^2 \rangle, \quad u \approx 0{\cdot}24 \text{ Å} .$$

This r.m.s. value would appear to be reasonable.

Accuracy of final model

The R_{21} value of the final structure model was 10·7% ($R_1 = 11{\cdot}1\%$) and the goodness-of-fit $k_{\Omega\Omega} = 0{\cdot}9886$; these values were obtained using a hydrogen atom scattering contribution, where the hydrogen atoms were placed at a distance of 1 Å from the carbons. The non-observed terms were included in the manner set out before.

It has become laudable practice to include in reports on finished structure investigations the r.m.s. errors in the coordinates and the density. Two main types of determination of the standard deviation are now in use: (*a*) Luzzati's method of graphical plots of R versus $\sin\theta$ (Luzzati, 1952); (*b*) Cruickshank's formulae (Cruickshank, 1949).

In our case Luzzati's graphs were not of direct applicability since his '*familles de courbes*' had been evaluated for clear-cut two- or three-dimensional cases, and our generalized procedure represented an intermediate case in that it employed partly higher-layer data. However, the Luzzati plot has the merit that it permits the user to ignore, as it were, large fluctuations in the outer $\sin\theta$ ranges (where the amplitudes are as a rule small, and therefore subject to great error in subjective estimation), and to extrapolate (admittedly in a somewhat arbitrary way) from the lower, reliable $\sin\theta$ ranges.

Cruickshank's formula, on the other hand, permitted us to employ used data in a direct computational way; it does, if used indiscriminately, tend to over-estimate the positional errors of the structure, since it enhances the error contributions of the sensitive reflexions with high indices, which, however, suffer from the estimation uncertainties.

We have tried to compromise between both methods in the following way: A graph was prepared of R_{21} versus $\sin\theta$, and a cut-off was introduced where the spots started to scatter erratically. The planes with a $\sin\theta$ value lower than the cut-off ($0{\cdot}75 = \sin\theta_c$) were then used for introduction into Cruickshank's formula. The non-observed terms of this range were included.

The mean value for parameter error thus found is $\sigma_{xz} \approx 0{\cdot}008$ Å, or a mean of $\sigma \approx 0{\cdot}012$ Å for the bond lengths and $\sigma \approx 1{\cdot}2°$ for the bond angles.

It has been pointed out to the author that there is a certain logical inconsistency in introducing this cut-off, since, after all, the entire range was used in the refinement operations. However, upon comparison of the formulae involved, it is seen again that the weight of the reflexions with high θ values is different in the differential synthesis as compared with the computation of the standard deviations, and we think that the procedure employed is permissible. The standard deviation of parameters, upon using the full range of data, becomes $\sigma_{xz} \approx 0{\cdot}009$ Å.

Cruickshank's formula, for this particular case, is

$$\sigma_x = \{\Sigma_H h^2 . \Delta F^2\}^{\frac{1}{2}} (a/2\pi) / \Sigma_H h^2 F_o . \mathrm{tr}\, hx_r . \mathrm{tr}\, lz_r \, ,$$

where F_o has the sign of F_c and the transcendental functions depend on the combination of h and l; x_r and z_r are the parameters of the atom for which the value σ_x is computed.

The structure-factor lists

The 263 processed planes are listed (Table 1) in sequential order of their (not printed) $\sin^2\theta$ value. These are all reciprocal-lattice points that are generated by copper radiation ($\lambda = 1{\cdot}5418$ Å) for the zero and first layer parallel to the b axis. The experimentally non-observed planes are marked, and an artifical F_o value is assigned, as described previously.

Discussion of the structure

The final parameters were found to be

O:	(1)	$x = 0{\cdot}1369$	$z = 0{\cdot}8041$
	(2)	0·3891	0·1376
	(3)	0·5151	0·3172
N:	(4)	0·2026	0·6838
	(5)	0·4237	0·2768
C:	(6)	0·3115	0·7131
	(7)	0·3823	0·5876
	(8)	0·3466	0·4169
	(9)	0·2348	0·3867
	(10)	0·1679	0·5184

The structural data, following from these parameters, are set out in Fig. 6. According to Cruickshank's suggestions of significance levels, all bonds in the molecule that are axially symmetrical do not differ significantly in length. The difference between the N–O bonds of the oxide group and the nitro group, however, is significant. The same is certainly also true for the C–N bonds in the ring and at the nitro group. Also, there appears to be a significant difference between the C–C distances in the ring, where they are not related by axial molecular symmetry.

The C–C bonds that are parallel to the axis of the molecule have about 90% double-bond character, and we are therefore justified in the assumption that quinoidal resonance structures are preponderant in the set of possible resonance models. The other C–C distances are longer than the bonds in benzene, and represent about 30% double-bond character. The C–N bonds of the ring have about 20% double-bond

Table 1. F_o *and* F_c *values*

Reflexions down to 4,0,10 are of the type *h*0*l*; the remaining reflexions are of the type *hll*.
A negative sign after the *l* column signifies that this reflexion is missing (non-observed)—see text.

All *F* values are multiplied by ten.

h	*l*	F_o	F_c
1	1	185	176
2		309	-304
2	1	558	-546
	2	535	547
1	2	77	73
3	1	155	153
2	2	125	-125
4		424	-423
4	1	46	-48
3	2	242	216
1	3	306	-315
4	2	132	-96
2	3	33	64
5	1	92	-54
3	3	99	-94
5	2	16	11
6		171	176
6	1	261	271
4	3	182	172
	4	115	-99
1	4	99	-76
2	4	49	19
6	2	33	6
5	3	86	-95
3	4	200	206
7	1	171	170
4	4	19	14
6	3	44	-21
7	2	44	15
1	5	132	149
8		121	135
5	4	157	-163
2	5	65	53
8	1	100	90
3	5	116	110
7	3	171	-192
8	2	30	25
6	4	76	84
4	5	56	-33
9	1	21	-23
8	3	135	-117
5	5	28	-16
7	4	146	-139
	6	42	68
9	2	93	-88
1	6	23	22
2	6	23	26
6	5	51	-71
3	6	220	-209
10		69	68
10	1	65	41
9	3	114	100
8	4	144	-169
4	6	48	52
10	2	116	-92
7	5 -	23	24
5	6	58	35
9	4	35	36
10	3	81	51
11	1	39	-22
1	7	162	-171
6	6	77	77
2	7	49	-57
6	5	79	-77
11	2	188	196
3	7	128	134
4	7	81	92
7	6	81	111
10	4	39	-10
11	3	35	-30
9	5	56	51
12	-	5	5
12	1	86	72
5	7	46	48
8	6	30	
12	2	42	36
6	7 -	5	5
	8	48	-51
11	4	69	-61
1	8	51	57
10	5	42	44
2	8 -	14	-14
12	3	37	-54
3	8	48	30
9	6 -	17	-17
13	1 -	4	4
7	7	33	-34
4	8 -	7	-7
13	2	32	29
11	5 -	5	-5
12	4	55	42
5	8 -	1	1
8	7	35	31
10	6	21	40
13	3	42	-43
6	8	74	-47
14	-	2	2
14	1	35	28
1	9	40	12
9	7	19	-2
14	2	60	-46
12	5	49	44
2	9	19	-15
7	8 -	2	-2
13	4	39	-28
11	6 -	4	4
3	9 -	18	-24
4	9 -	18	-30
14	3	32	-16
10	7 -	18	-18
8	8	18	-3
5	9 -	15	-15
15	1	46	36
13	5	32	22
12	6 -	10	-10
15	2	51	-39
14	4	30	25
6	9	25	8
9	8 -	14	14
11	7	28	-11
15	3 -	12	-12
	10	56	68
1	10 -	3	3
7	9	40	-29
2	10	55	-23
16	-	16	18
16	1 -	16	-29
14	5	53	-52
3	10 -	1	1
13	6 -	16	30
10	8 -	12	-12
4	10	16	-2
	1	115	118
1	1	520	-522
2		322	-307
2	1	550	540
1	2	64	-67
3	1	168	184
4		336	-354
4	1	225	213
3	2	241	260
	3	184	186
1	3	46	-41
4	2	38	70
2	3	339	-332
5	1	71	64
3	3	310	-326
5	2	362	354
6		259	262
6	1	191	-205
4	3	27	-42
1	4	85	-80
2	4	181	185
6	2	86	79
5	3	204	198
3	4	242	-264
7	1	46	-75
4	4	17	-33
6	3	61	79
7	2	31	-15
	5	85	-93
1	5	19	4
8		122	133
5	4	63	-86
8	1	99	93
2	5	33	-25
7	3	17	27
3	5	33	46
8	2	60	-71
6	4	168	-174
4	5	20	10
9	1	28	26
8	3	33	33
5	5	36	-34
7	4	119	103
1	6	110	94
9	2	101	-115
2	6	138	150
6	5	22	-14
3	6	20	32
10		99	100
10	1	27	
9	3	129	-139
8	4	53	50
4	6	58	-47
10	2	143	-145
7	5	68	-64
5	6	20	-9
9	4	107	-84
	7	102	-90
10	3	52	-31
1	7	93	63
11	1	52	62
6	6 -	5	5
8	5	68	-65
2	7	119	107
11	2	66	55
3	7	69	55
4	7	31	34
7	6	27	-40
10	4	27	25
11	3 -	16	-16
9	5	156	153
12		22	-34
12	1	101	86
5	7	22	-6
12	2 -	8	8
8	6	55	43
6	7 -	8	8
1	8 -	3	3
11	4	30	-24
10	5	20	-26
2	8	30	-32
12	3	30	-10
12	3 -	10	-10
3	8	36	-32
9	6	28	34
13	1	20	-9
7	7 -	17	-17
4	8 -	19	-20
13	2	42	45
11	5 -	1	-1
12	4 -	17	23
5	8	41	41
8	7 -	17	22
10	6 -	2	-2
13	3	39	-29
6	8 -	3	3
14		41	31
14	1 -		-
	9	44	31
9	7	42	-35
1	9	44	-33
14	2	35	12
2	9	25	-17
12	5 -	3	3
13	4	27	4
7	8 -	10	10
11	6 -	11	11
3	9 -	6	-6
4	9	38	-32
14	3 -	4	-4
10	7	31	19
8	8 -	4	4
5	9	28	-14
15	1 -	3	3
13	5 -	4	-4
12	6 -	5	5
15	2 -	12	12
14	4 -	7	-7
6	9	39	-28
9	8	24	9
11	7	19	14
15	3	20	-6
1	10 -	7	-7
7	9 -	2	-2
2	10 -	10	10
16	-	14	18
14	5 -	14	28
16	1 -	14	-16
3	10 -	4	4
13	6 -	12	12
10	8 -	14	-19

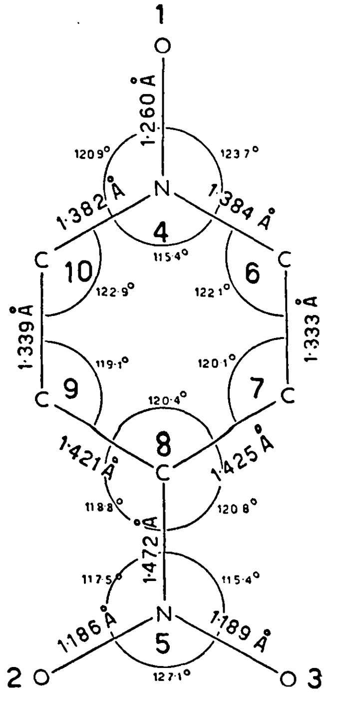

Fig. 6. Final bond lengths and bond angles as computed from ultimate parameters.

character and the C–N bond at the nitro group represents a pure single bond. The N–O oxide bond would then have 25% double-bond character and the N–O bonds of the nitro group about 70%.

It was thought to be somewhat unlikely that the C–N distance at the nitro group would indeed be a single bond; the r.m.s. error value allows for leeway towards a shorter bond. It must be stated, however, that even so the bond length was longer than anticipated whereas on the other hand the quinoidal C–C bonds proved to be much shorter than expected.

The separation of molecular layers is 3·02 Å and endorses the results of investigations of other aromatic nitro-substituted compounds. There does not appear to be van der Waals interaction between vicinary molecules. There is however a certain *vis-à-vis* positioning of the oxidic oxygen and hydrogens of the next molecule, but the distances are about 3·3 Å and no interaction (hydrogen bridges) can be deduced therefrom. There is the same order of separation in the nearest approach of molecules belonging to neighbouring layers, leading again to the conclusion that van der Waals bonds are absent, even discounting the argument that space-group symmetry requires the hydrogens to be in the planes $y = \frac{1}{4}$ and $y = \frac{3}{4}$. It is unlikely, if this were not so, that the space-group characteristics (extinctions) would be influenced noticeably.

An effort has been made to correlate data obtained from the 4-nitropyridine-*N*-oxide with X-ray studies carried out at present on other 4-substituted pyridine-*N*-oxides (Hayashi, 1950; McKeown, Ubbelohde & Woodward, 1951). These will be reported in more detail shortly.

The author is the recipient of a Fulbright Travel Grant and a George Ellery Hale Fellowship in the California Institute of Technology. He stands, moreover, in much obligation to Dr Linus Pauling, whose interest stimulated this research and who was good enough to read the manuscript. He is equally indebted to Drs Karst Hoogsteen, Edward W. Hughes and Robert Nathan for advice and discussions of some aspects of this project. He wishes especially to testify of his appreciation to Dr H. J. den Hertog of the Wageningen Agricultural Institute and to Dr Eiji Ochiai of the Pharmaceutical Institute of Tokyo University, whence most of the samples of pyridine-*N*-oxides have come.

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The Crystal and Molecular Structure of Bishydroxydurylmethane

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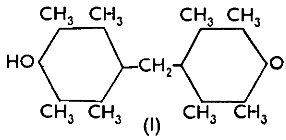
(*Received* 27 *February* 1956)

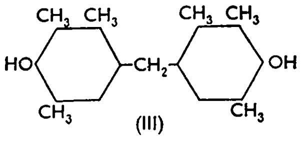
The structure of bishydroxydurylmethane has been fully determined. The crystals are monoclinic, with space group *C*2, and there are two molecules in a unit cell of dimensions $a = 22{\cdot}87$, $b = 4{\cdot}94$, $c = 7{\cdot}42$ Å and $\beta = 91° 0'$. Optical-transform methods have been used freely in the earlier stages of the structural analysis and the structure has been refined by two-dimensional Fourier syntheses. Steric repulsive interactions of the *o*-substituted methyl groups with the methylene group and of the *o*-substituted methyl groups with one another produce considerable strain in the molecule. Important features of the strain include a long $C_{Ar.}$–C_{CH_2} distance (1·60 Å), a wide angle (119°) between the two $C_{Ar.}$–C_{CH_2} linkages in each molecule and large displacements of the methylene carbon atom and the *o*-substituted methyl carbon atoms from the plane of the aromatic ring. The C–O distance is 1·35 Å.

1. Introduction

Bishydroxydurylmethane (I) can be hydrolysed and reduced with remarkable ease (Burawoy & Chamberlain, 1949); its behaviour in these respects is in marked contrast to that of bis-4-hydroxy-3:5-dimethylphenylmethane (II) and bis-4-hydroxy-2:3:5-trimethylphenylmethane (III), which often remain unchanged when subjected to similar chemical treatments. Burawoy & Chamberlain attribute the unusual activity of bishydroxydurylmethane to the weakening of the $C_{Ar.}$–C_{CH_2}–$C_{Ar.}$ linkages as a result of the intramolecular steric repulsive interaction of the *o*-substituted methyl groups with the methylene group and of the *o*-substituted methyl groups with one another. Because of the steric repulsion, it appears that any possible configuration of the bishydroxydurylmethane molecule must involve some



(I)



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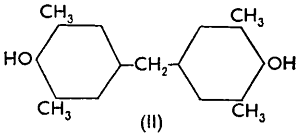

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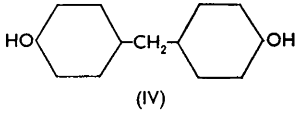

(IV)

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