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The Structure of the Free Radical di-*p*-Anisyl Nitric Oxide

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The unit cell of di-*p*-anisyl nitric oxide is orthorhombic, with $a = 7.33 \pm 0.04$, $b = 26.8 \pm 0.1$, $c = 6.25 \pm 0.03$ Å. The space group is *Aba2*, and in the unit cell there are four molecules, each lying on a twofold axis. The structure was solved by Fourier-transform methods, and the atomic positions, with bond lengths and angles, were found from the (100) and (001) Fourier projections.

Introduction

Di-*p*-anisyl nitric oxide is believed to be the first of the class of substances known as free radicals to be investigated by X-ray methods. This compound is quite stable, and the investigation, which depended largely on Fourier-transform methods, has presented no unusual difficulties.

Unit cell and space group

The sample supplied consisted of a mass of lath-like, red transparent crystals, from which it was not difficult to select single crystals suitable for X-ray examination. The unit cell was shown by oscillation photographs to be orthorhombic, and the unit-cell dimensions were found by considering the higher order $h00$, $0k0$ and $00l$ reflexions on *a*- and *c*-axis Weissenberg photographs. The results were:

$$a = 7.33 \pm 0.04, \quad b = 26.8 \pm 0.1, \quad c = 6.25 \pm 0.03 \text{ Å.}$$

A higher degree of accuracy is not claimed, since no allowance was made for film shrinkage.

The measured density of the sample was 1.33 ± 0.01 g.cm.⁻³, and the calculated density, corresponding to four molecules in the unit cell, was 1.32 ± 0.02 g.cm.⁻³.

The systematic absences were found to be: hkl for $k+l$ odd, $0kl$ for k odd or l odd, $h0l$ for h odd or l odd. These indicated the space group *Aba2* or *Abam*; packing considerations soon showed that the second of these was improbable, and the space group was assumed to be *Aba2*.

Determination of the structure

The X-ray intensities of the $hk0$ and $0kl$ zones were estimated by visual comparison of each Weissenberg

spot with a density wedge on similar film. The structure amplitudes were derived by using the usual trigonometrical factor; since the absorption coefficient of the substance was small, it was felt that further corrections were unnecessary.

The (100) projection, which showed the molecule roughly in plan, was solved by the Fourier-transform methods of Lipson & Taylor (1951). The problem was simplified by the fact that the space group *Aba2* has eight general positions, so that the four molecules were known to lie on twofold axes. In this projection, moreover, only one molecule had to be considered.

The projection was non-centrosymmetrical, and approximate phase angles were determined in a way which will be described in a subsequent paper on optical diffraction methods. The Fourier plot corresponding to these phase angles resolved every atom, and the projection was refined in the usual way by means of successive Fourier syntheses. This process was carried only as far as the fifth synthesis, as it then appeared that the suggested changes were becoming aimless. The (001) projection, which was centrosymmetrical, was then solved almost immediately by conventional methods.

Discussion of the structure

In Table 1 are given the atomic positions consistent with both projections, while in Tables 2 and 3 are compared the observed and calculated structure factors for the $0kl$ and $hk0$ zones. All the structure-factor calculations were carried out by the method of Beevers & Lipson (1952), using Fourier strips. The factor of agreement $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ is 0.15 for the $0kl$ zone, and 0.19 for the $hk0$ zone, although, if accidental absences in the zone are not considered,

Table 1. Atomic co-ordinates

Atom	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)
O ₁	0	0	-0.73
N ₁	0	0	1.17
C ₁	0.07	1.27	0.49
C ₂	0.59	2.35	1.19
C ₃	0.55	3.62	0.62
C ₄	-0.06	3.82	-0.58
C ₅	-0.61	2.74	-1.25
C ₆	-0.54	1.45	-0.70
C ₇	-0.06	5.10	-1.16
C ₈	-0.76	5.45	0.75

Table 2. Comparison of observed and calculated $F(0kl)$'s corresponding to one molecule

<i>Ok</i> l	F_o	F_c	α (°)
020	10.8	16.1	0
040	8.9	8.8	180
060	8.1	9.9	0
080	7.1	5.8	180
0,10,0	12.5	11.6	0
0,12,0	4.5	4.5	180
0,14,0	3.8	5.8	0
0,16,0	8.4	7.5	0
0,18,0	4.8	2.3	180
0,20,0	10.8	10.3	0
0,22,0	7.1	6.7	0
002	9.2	10.1	203
022	2.6	2.0	340
042	2.8	2.2	0
062	6.7	6.3	290
082	2.4	2.8	157
0,10,2	13.5	13.5	183
0,12,2	6.4	6.6	211
0,14,2	2.9	3.6	34
0,16,2	2.9	3.6	264
0,18,2	< 1.9	2.3	296
0,20,2	< 2.0	1.9	249
0,22,2	< 2.0	0.4	243
0,24,2	4.6	3.5	80
004	10.9	10.3	163
024	3.7	4.2	255
044	1.7	1.6	230
064	2.6	3.2	171
084	4.2	3.9	273
0,10,4	2.5	1.6	27
0,12,4	6.2	5.1	305
0,14,4	5.9	5.7	230
0,16,4	2.3	2.4	150
0,18,4	< 2.0	0.3	315
006	< 2.0	1.1	175
026	3.0	2.8	106
046	< 2.0	1.3	67
066	< 2.0	0.7	106
086	< 2.0	0.9	130
0,10,6	2.9	2.6	13
0,12,6	2.2	1.7	21
0,14,6	2.1	0.9	144

the latter figure drops to 0.17. Also, the calculated structure amplitude of the 020 reflexion is nearly 50% larger than the observed value, and this discrepancy cannot be much reduced by any small changes of atomic position. If this term is removed from consideration, however, along with any accidental absences within the two zones, the reliability factors become 0.13 for Ok l and 0.15 for hk 0.

Fig. 1 shows the electron-density maps of the (100)

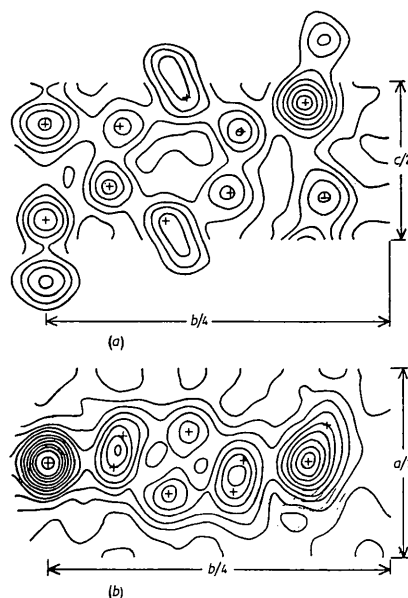


Fig. 1. Electron density maps of asymmetric unit. Contours are drawn at intervals of $1 \text{ e.}\text{\AA}^{-2}$, the lowest being $1 \text{ e.}\text{\AA}^{-2}$. (a) (100) projection. (b) (001) projection.

and (001) projections, corresponding to phase angles determined from the atomic positions of Table 1. Fig. 2 shows the arrangement, for each projection, of four molecules in a unit cell. It should be noted that in Fig. 2(b) the superimposed oxygen and nitrogen atoms lie on twofold axes, the symbols of which have been omitted for clarity.

Fig. 3 is the diagrammatic representation of the molecule, giving the bond lengths and angles, although

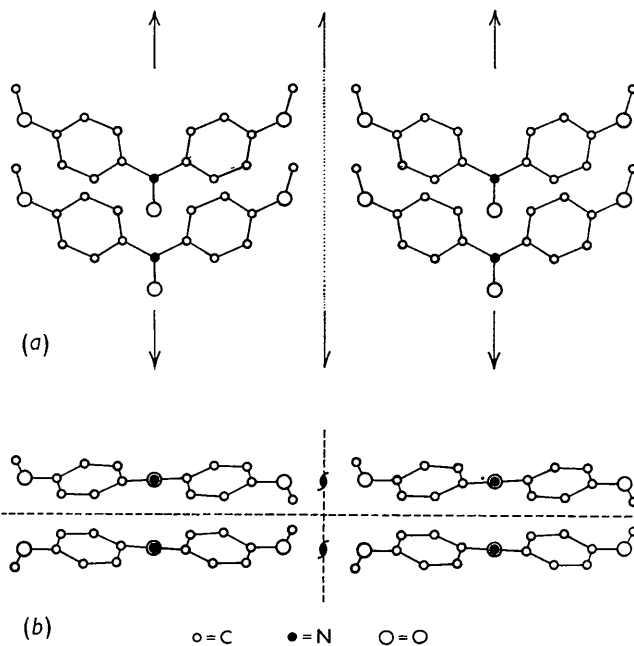


Fig. 2. Diagrammatic representations of four molecules in the unit cell. (a) (100) projection. (b) (001) projection.

Table 3. Comparison of observed and calculated $F(hk0)$'s corresponding to one molecule

$hk0$	F_o	F_c	$hk0$	F_o	F_c	$hk0$	F_o	F_c
020	10.9	16.1	220	7.8	10.0	420	< 1.8	3.4
040	9.3	-8.8	240	< 1.3	-0.2	440	6.5	5.0
060	8.6	9.9	260	9.2	11.7	460	10.6	9.8
080	7.3	-5.7	280	3.0	-2.1	480	< 2.0	0.7
0,10,0	10.9	11.4	2,10,0	5.0	5.4	4,10,0	< 2.1	-0.2
0,12,0	4.9	-4.5	2,12,0	2.8	-0.9	4,12,0	< 2.2	1.5
0,14,0	4.3	5.8	2,14,0	3.4	3.7	4,14,0	< 2.3	1.3
0,16,0	8.0	7.5	2,16,0	7.7	6.6	4,16,0	4.9	4.4
0,18,0	4.9	-2.3	2,18,0	< 2.2	-0.9	4,18,0	< 2.5	0.4
0,20,0	10.3	10.3	2,20,0	8.8	6.8	4,20,0	< 2.5	1.8
0,22,0	7.3	6.5	2,22,0	6.4	4.3	4,22,0	5.4	2.6
120	< 0.9	-2.5	320	< 1.5	-2.0	520	< 2.2	0.1
140	< 0.9	2.5	340	< 1.6	1.8	540	< 2.2	1.6
160	8.7	-8.0	360	8.4	8.4	560	< 2.3	-1.4
180	2.3	2.9	380	< 1.7	2.4	580	< 2.3	0.7
1,10,0	< 1.5	-0.2	3,10,0	< 1.8	0.2	5,10,0	< 2.4	0.7
1,12,0	3.0	-2.3	3,12,0	< 2.0	-2.8	5,12,0	< 2.4	-0.5
1,14,0	2.9	2.7	3,14,0	2.6	3.9	5,14,0	< 2.5	0.8
1,16,0	2.4	1.7	3,16,0	4.5	2.9	600	< 2.4	0.3
1,18,0	< 2.2	1.7	3,18,0	2.4	2.4	620	< 2.4	0.3
1,20,0	2.8	-2.3	3,20,0	4.3	-3.3	640	4.3	3.8
1,22,0	< 2.5	-1.9	3,22,0	3.6	-2.9	660	5.7	5.1
200	52.0	54.2	400	7.3	8.9			

in space the groups $C_6H_4OCH_3$ are tilted through approximately 33° about the line C_1C_4 . It is perhaps worth remarking that none of the atoms O_1 , N, C_1 , C_4

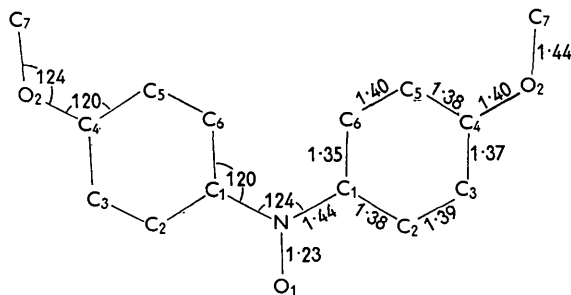


Fig. 3. Diagrammatic representation of molecule, showing bond lengths (in Angstrom units) and angles (in degrees).

and O_2 lies more than 0.07 \AA out of the plane of projection.

It is felt that the bond lengths should be in error by no more than 0.05 \AA , and the bond angles by no more than 5° . The only quantity calling for comment is the angle $C_4-O_2-C_7$ ($C-O-CH_3$), for which the observed value of 124° is much higher than the tetrahedral angle of about 109° . While it is not claimed that

the X-ray data are particularly accurate, or even that the process of refinement has been carried to the limit, it is difficult to believe that the experimental error is sufficient to account for such a difference. The projections available are not, however, ideal for determining this angle and it is felt that three-dimensional methods would be necessary to settle the point.

The X-ray investigation was greatly facilitated by the high quality of the sample of di-*p*-anisyl nitric oxide. The author wishes to thank Mr F. Liversedge, of the Chemistry Department, College of Technology, who prepared the sample, and Dr A. Burawoy, of the same department, who allowed its use, and who contributed much helpful discussion. Thanks are also due to Drs H. Lipson and C. A. Taylor, of the Physics Department, College of Technology, for valuable advice and encouragement, and to the Canadian Department of Veterans' Affairs for a maintenance grant.

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