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The Crystal Structure of *p*-Azoxyanisole

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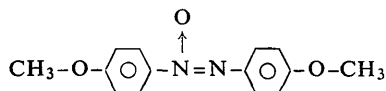
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The stable crystalline form of *p*-azoxyanisole is assigned to space group $P2_1/a$ (C_{2h}^5) with four molecules in the unit cell having parameters $a=15.776$, $b=8.112$, $c=11.018$ Å and $\beta=114.57^\circ$. The crystal structure was refined by full-matrix least-squares to a final R value of 0.091 using 2507 reflections measured with a manually operated single-crystal diffractometer. The molecules are arranged in the unit cell with their long axes approximately perpendicular to the (100) plane. The angle between the normals to the two benzene rings is 22.6° , and the $-N=N-$ bond conformation departs from the planar *trans* position by approximately 4.2° .

Introduction

Bernal & Crowfoot (1933) observed that despite the numerous studies of the mesomorphic behavior of liquid crystals, rather little attention had been paid to the crystalline structures of these compounds. They reported the analysis of several mesomorphic compounds, such as *p*-azoxyanisole, *p*-azoxyphenetole, 1,5-di(*p*-methoxybenzylideneamino)naphthalene, and several cinnamate compounds. Their studies, however, were performed over thirty years ago and provided structures which accounted for the optical properties but only qualitatively for the X-ray intensities. A knowledge of the complete crystal structure would obviously be of considerable assistance in interpreting diffraction studies performed upon the mesophase, which can exhibit interesting physical properties. For example, Falgueirettes (1959) and Kosterin & Chistyakov (1968) have studied the nematic liquid crystalline phase aligned by a magnetic or electric field.

Among the substances which melt to form a nematic mesophase, *p*-azoxyanisole:



has been most frequently selected for study. Bernal & Crowfoot (1933) noted the existence of two crystalline

modifications of this compound, a stable yellow form and an unstable white polymorph. More recently, Robinder & Poirier (1968) have demonstrated the existence of two monotropic crystalline phases of *p*-azoxyanisole in addition to the form which is stable at room temperature. This paper reports the refinement and crystal structure of the stable form of *p*-azoxyanisole.

Experimental

Single crystals of *p*-azoxyanisole were obtained as prisms by slow evaporation of an *n*-heptane solution. All measurements were performed using a manual Picker diffractometer, nickel-filtered copper radiation, and a scintillation counter with a pulse-height analyzer. The unit-cell parameters are: $a=15.776 \pm 0.012$, $b=8.112 \pm 0.005$, $c=11.018 \pm 0.009$ Å and $\beta=114.57^\circ \pm 0.04^\circ$ using $\text{Cu } K\alpha_1=1.5405$ and $\text{Cu } K\alpha_2=1.5443$ Å. Systematic absences of $h0l$ for h odd, and of $0k0$ for k odd, indicate the space group is $P2_1/a$ (C_{2h}^5). The density calculated for four molecules per unit cell is 1.337 g.cm^{-3} , which is in reasonable agreement with 1.348 g.cm^{-3} observed by Würstlin (1934). Transformation of the unit-cell parameters reported by Bernal & Crowfoot (1933), and by Würstlin (1934) to our convention permits the comparison shown in Table 1. Our parameters agree closely with those of Bernal & Crowfoot. The unit cell of Würstlin has a volume twice as large as ours, and we were unable to find the additional reflections reported by Würstlin which would require the larger unit cell.

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Table 1. Unit-cell parameters for *p*-azoxyanisole in space group $P2_1/a$

| | This work | Bernal & Crowfoot | Würlin |
|-----------------|-------------------------------|-------------------|----------|
| $a(\text{\AA})$ | 15.776 ± 0.012 | (15.67) | (16.0) |
| $b(\text{\AA})$ | 8.112 ± 0.015 | (8.10) | (8.08) |
| $c(\text{\AA})$ | 11.018 ± 0.009 | (11.0) | (21.9) |
| β | $114.57^\circ \pm 0.04^\circ$ | (114.5°) | (116.7°) |

Intensity measurements were performed using the method described by Alexander & Smith (1961). Prism-shaped crystals were ground to an approximately spherical shape. The crystal used for intensity measurements was $0.4 \times 0.4 \times 0.5$ mm. Peak intensities were measured for all reflections in the sphere $2\theta < 150^\circ$. The ratios of integrated to peak intensities were carefully measured for 50 reflections. These ratios varied smoothly with 2θ , and showed no evident anisotropy with the direction of the reflecting plane. This function was used to convert the measured peak intensities to integrated intensities. Corrections were applied for background scattering and counter loss, but no correction was made for absorption. The F values of 54 of the 2561 non-equivalent reflections within the sphere $2\theta < 150^\circ$ were set equal to zero, and were not included in the refinement. Intensities calculated from the final structure for these 54 reflections were at, or below, the observable threshold value.

Structure analysis

Comparison of the three-dimensional sharpened Patterson map with a model constructed using normal bond distances and angles indicated that the molecule was nearly fully extended, with its long axis tilted about 10° from the $(10\bar{1})$ plane and about 20° from the (010) plane. Furthermore, the benzene rings were inclined to the (010) plane.

The $(h0l)$ projection was examined next. Successive structure factor, Fourier, and difference Fourier cal-

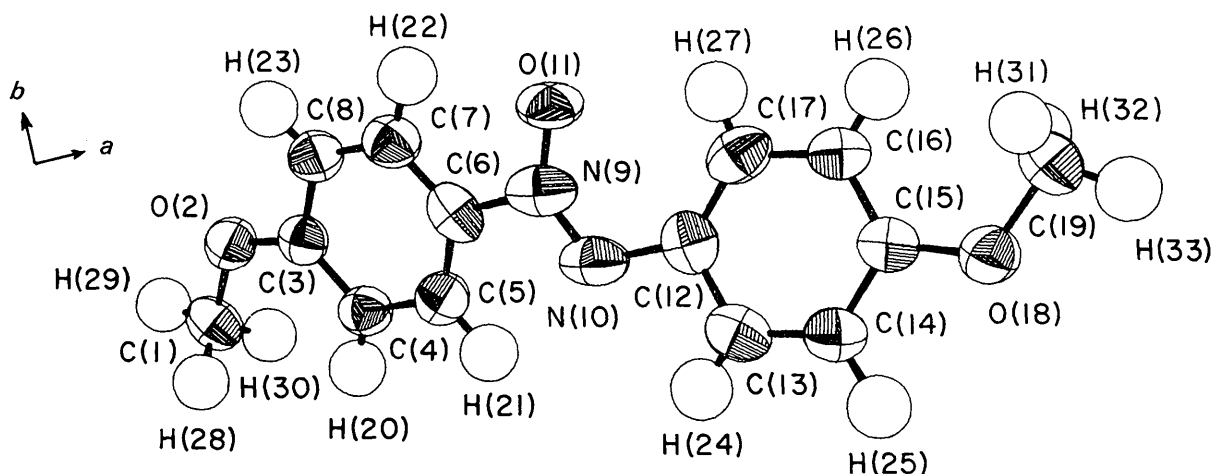
culations reduced the R index to 0.18 for all $h0l$ reflections using a uniform isotropic temperature factor $B = 4.96 \text{ \AA}^2$.

After obtaining approximate values for the x and z coordinates, a calculation of $F(hkl)$ was performed. Here two distinct models, having coordinates x, y, z and $x + \frac{1}{4}, y', z$, were employed because from the $(h0l)$ projection alone it is impossible to distinguish a center of symmetry from a twofold screw axis along b . Structure factor calculations resulted in R values of 0.46 for the first model, and 0.62 for the second. Further refinement was therefore performed using the former.

Three cycles of differential synthesis, allowing only shifts of the y coordinates of the nineteen non-hydrogen atoms, and using a uniform isotropic temperature factor, reduced R from 0.46 to 0.23. Two further cycles using individual isotropic temperature factors, and allowing variation of all coordinates, reduced R to 0.18.

When the positions of the non-hydrogen atoms and their anisotropic temperature factors were refined using full-matrix least squares, the R index decreased to 0.12. A difference Fourier synthesis, using structure factors calculated without hydrogen atoms, clearly showed well rounded peaks representing the fourteen hydrogen atoms with electron densities ranging between 0.5 and 0.7 e. \AA^{-3} . The hydrogen atom positions were estimated from the maxima of these peaks. Upon inserting these hydrogen atoms in the structure, and allowing all positions and anisotropic temperature factors to vary, the R index decreased to its final value of 0.091. Refinement was terminated when the standard deviation exceeded nearly all of the shift magnitudes. Examination of the coordinates revealed that the final hydrogen atom positions were structurally reasonable.

The weights used in the final stages of least-square refinement were calculated from $\sigma^2 = 0.454 + 0.061 |F_o| + 0.008 |F_o|^2$, where the coefficients were selected so that $\langle \sum w ||F_o| - |F_c||^2 \rangle$ remained invariant with $\langle |F_o| \rangle$.

Fig. 1. Perspective drawing of the *p*-azoxyanisole molecule with thermal ellipsoids.

The difference Fourier synthesis showed only two extraneous peaks with electron densities greater than $0.2 \text{ e. } \text{\AA}^{-3}$. These two peaks, having electron densities $0.7 \text{ e. } \text{\AA}^{-3}$, are located in the plane of the azoxy group, and nearly perpendicular to the nitrogen double bond. Because of their positions these cannot represent hydrogen atoms. One possibility is that the structure is slightly disordered as a result of a small percentage of the molecules entering the crystal with the two nitrogen atoms reversed. This type of disorder has been observed in *p*-azotoluene by Brown (1966*b*). By appropriate rotations one can achieve approximate superposition of all of the atoms except the two nitrogen atoms, which are then located near the positions of the two extraneous peaks in the difference map.

Fig. 1 shows a perspective drawing of the molecular structure with atomic labels, while Tables 2 and 3 list the final fractional atomic coordinates and temperature factors, along with their standard deviations.

Description of the structure

Bond distances and angles

The bond distances and angles are listed in Table 4. The two benzene rings have carbon bond distances averaging 1.384 ± 0.010 and $1.385 \pm 0.015 \text{ \AA}$, and quite reasonable C—C bond angles averaging $120.0 \pm 0.7^\circ$. The average aromatic bond lengths are somewhat short, perhaps as a result of thermal motion. We have not attempted to apply the correction proposed by Cruickshank (1961). The nitrogen—nitrogen bond length, $1.218 \pm 0.005 \text{ \AA}$, indicates considerable double-bonded character. This is shorter than the value, 1.243 \AA , reported for *p*-azotoluene (Brown, 1966*b*), and falls near the average of the values for the two molecules in

Table 2. Atomic coordinates of *p*-azoxyanisole

| | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|-------|----------------|---------------|--------------|
| C(1) | −0.23311 (28)* | −0.04705 (54) | 0.48652 (44) |
| O(2) | −0.18465 (17) | 0.08853 (31) | 0.46132 (25) |
| C(3) | −0.09467 (23) | 0.11463 (39) | 0.54570 (33) |
| C(4) | −0.04312 (25) | 0.01732 (46) | 0.65615 (34) |
| C(5) | 0.04985 (26) | 0.05669 (47) | 0.73317 (35) |
| C(6) | 0.08950 (24) | 0.19123 (41) | 0.69894 (34) |
| C(7) | 0.03868 (28) | 0.28628 (45) | 0.58969 (40) |
| C(8) | −0.05281 (28) | 0.24810 (46) | 0.51327 (41) |
| N(9) | 0.18922 (25) | 0.23966 (35) | 0.77533 (31) |
| N(10) | 0.22817 (26) | 0.15249 (37) | 0.87293 (33) |
| O(11) | 0.22030 (19) | 0.36082 (30) | 0.73160 (27) |
| C(12) | 0.33006 (25) | 0.18597 (44) | 0.94867 (36) |
| C(13) | 0.36329 (29) | 0.10634 (47) | 1.07232 (40) |
| C(14) | 0.45643 (26) | 0.10696 (45) | 1.15318 (36) |
| C(15) | 0.51990 (24) | 0.18355 (38) | 1.11352 (31) |
| C(16) | 0.48810 (27) | 0.26231 (45) | 0.99162 (35) |
| C(17) | 0.39226 (30) | 0.26357 (50) | 0.91016 (37) |
| O(18) | 0.61080 (17) | 0.17329 (32) | 1.20136 (23) |
| C(19) | 0.67989 (27) | 0.24368 (55) | 1.16339 (44) |
| H(20) | −0.0697 (33) | −0.0737 (65) | 0.6834 (48) |
| H(21) | 0.0863 (31) | −0.0217 (62) | 0.8123 (47) |
| H(22) | 0.0747 (33) | 0.3827 (63) | 0.5664 (48) |
| H(23) | 0.0910 (35) | 0.3180 (63) | 0.4378 (50) |
| H(24) | 0.3170 (33) | 0.0437 (61) | 1.0878 (47) |
| H(25) | 0.4865 (32) | 0.0490 (61) | 1.2551 (48) |
| H(26) | 0.5335 (33) | 0.3178 (61) | 0.9629 (48) |
| H(27) | 0.3794 (33) | 0.3193 (61) | 0.8294 (49) |
| H(28) | −0.2364 (31) | −0.0303 (60) | 0.5876 (48) |
| H(29) | −0.2952 (34) | −0.0426 (62) | 0.4061 (49) |
| H(30) | −0.1986 (34) | −0.1634 (63) | 0.4818 (48) |
| H(31) | 0.6667 (33) | 0.3659 (66) | 1.1508 (48) |
| H(32) | 0.6722 (33) | 0.1934 (61) | 1.0740 (51) |
| H(33) | 0.7427 (30) | 0.2020 (55) | 1.2354 (43) |

* Numbers in parentheses give the standard deviations in the last significant figures.

the asymmetric unit of *trans*-azobenzene, 1.243 and 1.173 \AA . Earlier work gave 1.23 \AA for *cis*-azobenzene

Table 3. Temperature factors for the expression $\exp[-2\pi^2(U_{11}h^2a^*2 + 2U_{12}hka^*b^* + \dots)]$

Coefficients $\times 10^4$.

Temperature factors assigned to hydrogen were $B_{11} = B_{22} = B_{33} = 0.0747$, $B_{12} = B_{23} = 0$, and $B_{31} = 0.0309$.

| | U_{11} | U_{22} | U_{33} | U_{12} | U_{23} | U_{31} |
|-------|-----------|----------|----------|-----------|-----------|----------|
| C(1) | 691 (23)* | 741 (24) | 827 (24) | −149 (19) | −87 (20) | 382 (19) |
| O(2) | 617 (14) | 675 (14) | 766 (15) | 0 (11) | 94 (12) | 241 (12) |
| C(3) | 643 (19) | 485 (16) | 628 (18) | 36 (14) | −50 (14) | 339 (15) |
| C(4) | 704 (21) | 609 (19) | 619 (18) | 13 (16) | 3 (15) | 324 (16) |
| C(5) | 719 (22) | 692 (21) | 563 (17) | 77 (17) | −32 (16) | 287 (16) |
| C(6) | 631 (19) | 581 (18) | 705 (19) | −124 (15) | −281 (15) | 372 (16) |
| C(7) | 780 (24) | 543 (18) | 823 (23) | −23 (17) | 2 (17) | 409 (20) |
| C(8) | 717 (22) | 563 (19) | 811 (23) | −1 (16) | 59 (17) | 346 (19) |
| N(9) | 1156 (25) | 499 (15) | 703 (17) | 13 (15) | −32 (14) | 573 (17) |
| N(10) | 1103 (25) | 553 (16) | 807 (19) | 67 (16) | 93 (14) | 608 (19) |
| O(11) | 852 (17) | 561 (13) | 834 (16) | −171 (12) | 158 (12) | 350 (14) |
| C(12) | 659 (20) | 621 (19) | 670 (19) | 5 (16) | −159 (16) | 300 (17) |
| C(13) | 812 (25) | 635 (20) | 778 (22) | −95 (18) | −87 (17) | 439 (20) |
| C(14) | 740 (22) | 623 (19) | 661 (20) | −49 (17) | 33 (16) | 320 (17) |
| C(15) | 691 (20) | 472 (15) | 574 (17) | −40 (14) | −72 (13) | 303 (15) |
| C(16) | 738 (21) | 634 (19) | 593 (17) | −32 (17) | 27 (15) | 310 (16) |
| C(17) | 917 (27) | 707 (22) | 552 (19) | 107 (19) | 35 (17) | 283 (19) |
| O(18) | 652 (14) | 744 (15) | 599 (13) | −68 (12) | 26 (11) | 222 (11) |
| C(19) | 685 (22) | 736 (24) | 852 (25) | −109 (18) | −67 (20) | 364 (20) |

* Numbers in parentheses give the standard deviations in the last significant figures.

Table 4. *The bond distances and angles and their standard deviations*

| | Distance | σ | | Angle | σ |
|-------------|----------|----------|-------------------|-------|----------|
| C(1)—O(2) | 1.431 | 0.0051 | C(1)—O(2)—C(3) | 118.7 | 0.30 |
| O(2)—C(3) | 1.352 | 0.0045 | O(2)—C(3)—C(4) | 125.2 | 0.31 |
| C(3)—C(4) | 1.394 | 0.0051 | O(2)—C(3)—C(8) | 114.9 | 0.33 |
| C(4)—C(5) | 1.392 | 0.0056 | C(4)—C(3)—C(8) | 119.9 | 0.35 |
| C(5)—C(6) | 1.386 | 0.0053 | C(3)—C(4)—C(5) | 119.1 | 0.34 |
| C(6)—C(7) | 1.372 | 0.0055 | C(4)—C(5)—C(6) | 119.7 | 0.35 |
| C(7)—C(8) | 1.370 | 0.0062 | C(5)—C(6)—C(7) | 121.1 | 0.37 |
| C(3)—C(8) | 1.390 | 0.0052 | C(5)—C(6)—N(9) | 122.8 | 0.33 |
| C(6)—N(9) | 1.496 | 0.0053 | C(7)—C(6)—N(9) | 116.1 | 0.32 |
| N(9)—N(10) | 1.218 | 0.0047 | C(6)—C(7)—C(8) | 119.6 | 0.37 |
| N(9)—O(11) | 1.279 | 0.0042 | C(7)—C(8)—C(3) | 120.6 | 0.38 |
| N(10)—C(12) | 1.496 | 0.0056 | C(6)—N(9)—N(10) | 111.8 | 0.33 |
| C(12)—C(13) | 1.398 | 0.0058 | C(6)—N(9)—O(11) | 117.9 | 0.31 |
| C(13)—C(14) | 1.365 | 0.0061 | N(10)—N(9)—O(11) | 130.3 | 0.38 |
| C(14)—C(15) | 1.394 | 0.0054 | N(9)—N(10)—C(12) | 114.7 | 0.34 |
| C(15)—C(16) | 1.380 | 0.0051 | N(10)—C(12)—C(13) | 109.9 | 0.34 |
| C(16)—C(17) | 1.401 | 0.0061 | N(10)—C(12)—C(17) | 130.6 | 0.36 |
| C(12)—C(17) | 1.373 | 0.0060 | C(13)—C(12)—C(17) | 119.1 | 0.38 |
| C(15)—O(18) | 1.359 | 0.0045 | C(12)—C(13)—C(14) | 120.0 | 0.39 |
| O(18)—C(19) | 1.438 | 0.0051 | C(13)—C(14)—C(15) | 121.0 | 0.36 |
| | | | C(14)—C(15)—C(16) | 119.6 | 0.36 |
| | | | C(14)—C(15)—C(18) | 115.6 | 0.31 |
| | | | C(16)—C(15)—O(18) | 124.8 | 0.34 |
| | | | C(15)—C(16)—C(17) | 119.1 | 0.37 |
| | | | C(16)—C(17)—C(12) | 121.2 | 0.37 |
| | | | C(15)—O(18)—C(19) | 118.1 | 0.30 |

(Hampton & Robertson, 1941) and *trans*-azobenzene (De Lange, Robertson & Woodward, 1939), and 1.31 Å for the *p*-dibromonitrosobenzene dimer (Darwin & Crowfoot-Hodgkin, 1950). The nitrogen–oxygen bond length was found to be 1.279 ± 0.004 Å, which may be compared with 1.31 Å for the *p*-dibromonitrosobenzene dimer (Darwin & Crowfoot-Hodgkin, 1950), 1.25 Å for *trans*-dinitrosomethane (Van Meerssche & Leroy, 1959), and 1.31 Å for *cis*-nitrosomethane (Germain, Pirot & Van Meerssche, 1963). The carbon–hydrogen distances are reasonable, ranging from 0.94 to 1.12 Å. The shortest intermolecular distances are given in Table 5.

Table 5. *Shortest intermolecular distances*

| | | |
|---------------|--------|------------------------|
| C(19)···O(2) | 3.33 Å | <i>a</i> ··· <i>a'</i> |
| O(2)···C(1) | 3.37 | <i>a</i> ··· <i>c</i> |
| C(1)···O(11) | 3.43 | <i>a</i> ··· <i>d</i> |
| O(2)···C(6) | 3.57 | <i>a</i> ··· <i>b</i> |
| O(18)···O(2) | 3.38 | <i>a</i> ··· <i>a'</i> |
| C(4)···C(8) | 3.57 | <i>a</i> ··· <i>b</i> |
| C(13)···C(19) | 3.64 | <i>a</i> ··· <i>d</i> |
| C(5)···C(16) | 3.68 | <i>a</i> ··· <i>d</i> |
| C(4)···C(7) | 3.68 | <i>a</i> ··· <i>b</i> |
| C(3)···C(6) | 3.69 | <i>a</i> ··· <i>b</i> |
| C(1)···N(9) | 3.59 | <i>a</i> ··· <i>b</i> |
| N(10)···C(19) | 3.68 | <i>a</i> ··· <i>d</i> |
| O(1)···H(28) | 2.40 | <i>a</i> ··· <i>d</i> |
| H(33)···O(2) | 2.46 | <i>a</i> ··· <i>a'</i> |

$$\begin{aligned}
 a: & x, y, z \\
 a': & 1+x, y, 1+z \\
 b: & -x, -y, 1-z \\
 c: & \frac{1}{2}-x, \frac{1}{2}+y, 1-z \\
 d: & \frac{1}{2}+x, \frac{1}{2}-y, z
 \end{aligned}$$

The angle N(10)—C(12)—C(17), 130.6° , is significantly larger than the normal value. A similarly large

value for this angle has been obtained for the *p*-azoxyanisole mercurichloride adduct (McPhail & Sim, 1969). The angle, 130.3° , at N(9)—N(10)—O(11) is also larger than normal, perhaps because of the repulsion between O(11) and H(27) on C(17). There seems to be little evidence for the existence of hydrogen bonds between O(11) and H(22) and H(27) except the small distance of closest approach, 2.27 and 2.31 Å, respectively.

Molecular conformation

The equation for the least-squares best plane representing the benzene ring composed of C(3) through C(8) relative to the crystal axes is

$$0.5672x - 0.5904y - 0.5742z = 5.5904$$

and the displacements from this plane are

$$\begin{aligned}
 \text{C(3)} & -0.0035; & \text{C(4)} & +0.0014; & \text{C(5)} & +0.0014; \\
 \text{C(6)} & -0.0023; & \text{C(7)} & +0.0002; & \text{C(8)} & +0.0027 \text{ \AA}.
 \end{aligned}$$

The best plane for ring C(12) through C(17) has the equation

$$0.3099x - 0.8481y - 0.4298z = 5.1011$$

with displacements

$$\begin{aligned}
 \text{C(12)} & +0.0025; & \text{C(13)} & +0.0046; & \text{C(14)} & -0.0073; \\
 \text{C(15)} & +0.0030; & \text{C(16)} & +0.0040; & \text{C(17)} & -0.0067 \text{ \AA}.
 \end{aligned}$$

The standard deviations of the displacements for both rings range from 0.0035 to 0.0042, while the average displacement of an atom from the mean plane is 0.0019 for the first ring and 0.0047 Å for the second.

One might expect the azoxy group to adopt a planar *trans* conformation; however, the equation of the plane through atoms C(6), N(9) and N(10) is

$$0.5469x - 0.6312y - 0.5500z = 5.8100$$

and the displacement of O(11) from this plane is only -0.0017 \AA , while the displacement of C(12) from the plane is $+0.1005 \text{ \AA}$, which is approximately twenty-five times the standard deviation, 0.0038 \AA . The bonds of $-\text{N}(9)=\text{N}(10)-$ appear to be twisted away from the planar *trans* form by 4.2° . The angle between the normals of the two benzene rings is 22.6° , benzene ring C(3) through C(8) being rotated 3.0° from the plane of C(6)-N(9)-N(10), while the other ring is rotated 19.7° from the same plane. Evidently the energy gained by π -orbital overlap is sufficient to permit deformation of some of the bond angles from their normal values, and to cause the close approach of O(11) to H(22) and H(27).

Molecular arrangement

The molecular arrangement of crystalline *p*-azoxyanisole is shown in the packing diagram, Fig. 2. The nearly extended molecules are arranged approximately perpendicular to the (100) plane. The proximity of the ether group of one molecule and $-\text{N}=\text{N}-$ of its neighbor is a feature shared with anisaldazine (Galigné & Falgueirettes, 1968) and *p*-azophenetole (Galigné & Falgueirettes, 1969), both of which also form a nematic liquid crystal phase on fusion. This imbricated structure is the basic packing required for nematic behavior according to Gray (1962).

A recent abstract (Carlisle & Smith, 1969) indicates that these authors have analyzed the crystal structures of both *p*-azoxyanisole and *p*-azoxyphenetole. Both

structures are reported to exhibit a 'statistical' disorder involving displacement of the molecules parallel to their long axes. In our experience the extent of this disorder, as judged by 'smear' lines on X-ray photographs, varies considerably from crystal to crystal. It is also interesting in this connection that the thermal ellipsoids shown in Fig. 1 do not appear to be particularly elongated in the direction of the molecular axis, nor does the difference Fourier synthesis furnish any evidence for this type of disorder in the particular crystal selected for our study.

Work is currently in progress on the stable form of a typical smectogenic compound, ethyl *p*-azoxybenzoate.

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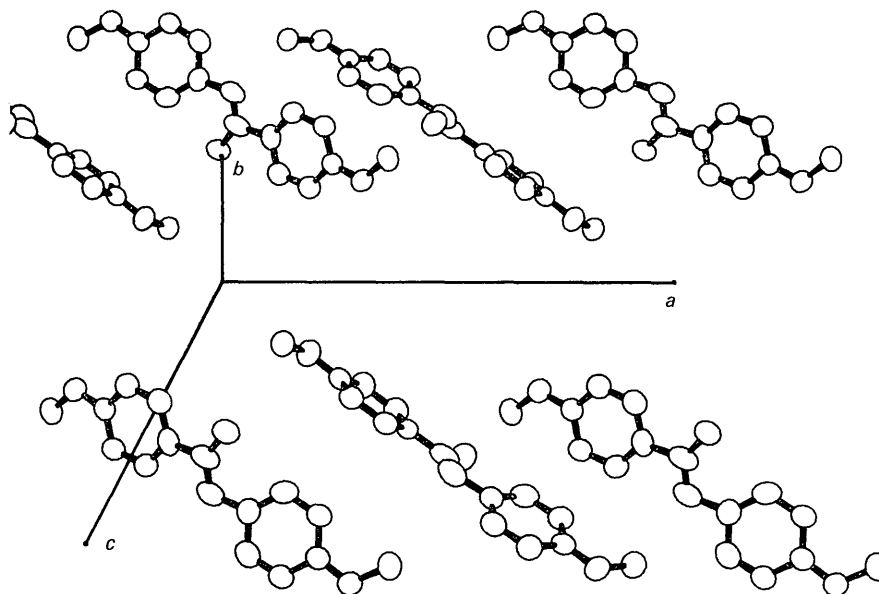


Fig. 2. Packing diagram for *p*-azoxyanisole.

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A Refinement of the Structure of Barium Tantalum Oxide, $\text{Ba}_5\text{Ta}_4\text{O}_{15}$

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The five-layer structure previously reported for $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ has been confirmed. An isotropic structure refinement was carried out with 253 counter-recorded reflections larger than 2σ for their background to a conventional R value of 5.7%. Anomalous dispersion, absorption, and secondary extinction corrections were made. The space group is $P\bar{3}m1$; cell dimensions are $a = 5.776 \pm 0.005$, $c = 11.82 \pm 0.01$ Å, and there is one formula unit per cell. The octahedral environments of the tantalum atoms are distorted in a manner consistent with the requirements of local charge balance. The shortest Ta–O distances in the octahedra are 1.86 ± 0.02 Å, the longest are 2.22 ± 0.03 Å. The shortest Ba–O distance is 2.64 ± 0.03 Å.

Introduction

The preparation and structure of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and the related compounds $\text{Sr}_5\text{Ta}_4\text{O}_{15}$, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ and the oxygen deficient compounds $\text{Ba}_5\text{Ta}_4\text{O}_{13}$ and $\text{Ba}_5\text{Nb}_4\text{O}_{13}$ were reported by Galasso & Katz (1961). The structure determination was based on data for $\text{Ba}_5\text{Ta}_4\text{O}_{15}$, but since even the longest exposure – a 30° precession photograph which ran for 22 days – showed less than half of the possible $h0l$ reflections, it was considered impractical then to collect more than the 88 observed reflections recorded. As a result, oxygen positions had to be inferred, though there seemed to be no doubt as to the essential correctness of the proposed structure. Since the time it was first reported, the structure has been shown to be quite stable. Under certain conditions the compound $\text{Ba}_3\text{SrTa}_3\text{O}_9$ undergoes chemical change producing $(\text{Ba}, \text{Sr})_5\text{Ta}_4\text{O}_{15}$ as one of the products (Galasso, Barrante & Katz, 1961). Also some of the compounds containing rhenium with ordered perovskite structures reported by Sleight, Longo & Ward (1962) were found to be unstable when heated in air at 1000°C ; the products obtained in many instances have a structure of the $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ type. A refinement of this structure has now been carried out which permits a more detailed description than was possible before, even though it was still not possible to collect a large set of data.

Experimental

The preparation $5\text{BaCO}_3 + 2\text{Ta}_2\text{O}_5 \rightarrow \text{Ba}_5\text{Ta}_4\text{O}_{15} + 5\text{CO}_2$ yielded a tan-colored product when carried out in air at 1100°C . This tan compound produced a powder pattern identical to that reported by Galasso for $\text{Ba}_5\text{Ta}_4\text{O}_{15}$. Well formed platy crystals were then grown from a lead(II) oxide flux.

The best crystal available for study was a thin hexagonal plate, 0.014 mm thick and 0.106 mm between opposite faces of the hexagonal prism. The crystal was mounted with the a^* axis parallel to the fiber axis. Precession photographs confirmed the previously reported Laue group $\bar{3}m$ and were consistent with the assigned space group $P\bar{3}m1$.

Cell dimensions and intensities were measured on a General Electric XRD-5 diffractometer equipped with a single-crystal orienter. Lattice constants were determined by averaging results from high order $h00$ and $h0l$ reflections and were found to be $a = 5.776 \pm 0.005$, $c = 11.82 \pm 0.01$ Å. Intensities were measured on the orienter with Zr-filtered Mo radiation, pulse height selection, and a scintillation counter by the moving-crystal moving-counter method. Background was determined from 20 second counts on both sides of the 80 second 2.66° scan. A standard reflection monitored daily showed an overall variation of less than 2%. Intensities were collected for all $h \geq 0$, $k \geq 0$, $0 \leq l \leq 6$.