

## The Structure of Arsenobenzene\*

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An X-ray diffraction study of monoclinic crystals of arsenobenzene has shown that the molecule is not a dimer, as given in many text books, but is a hexamer,  $\text{As}_6\varphi_6$ . The arsenic atoms are arranged in a six-membered ring which has the 'chair form'. The As-As distances are  $2.456 \pm 0.005$  Å and the As-As-As angles average  $91^\circ$ . The phenyl groups are attached to arsenic atoms in the 'radial' positions. The molecule has only a center of symmetry but does not deviate greatly from the symmetry  $\bar{3}2/m$ . The packing of the molecules in the crystal involves only phenyl to phenyl contacts.

Most text books ascribe to arsenobenzene and its important pharmaceutical derivative arsphenamine ('salvarsan') a structure involving doubly bonded arsenic atoms. Thus, arsenobenzene itself is usually written as  $\varphi\text{-As}=\text{As}-\varphi$ . Prof. Pauling pointed out to us many years ago that this structure was highly improbable because of the reluctance of elements outside the first row of the periodic table to form double bonds. Molecular weight determinations (Palmer & Scott, 1928; Blicke & Smith, 1930) in solution have suggested polymerized molecules containing an average of from 2.2 to 6.0 arsenic atoms each, but the values are so scattered and contradictory as to be inconclusive. Since crystals of arsenobenzene are readily obtainable it was decided to carry out a structure determination by X-ray diffraction. The principal experimental work was completed and a good trial structure obtained by early 1949, and preliminary reports were presented to the American Society for X-ray and Electron Diffraction Meeting, Ithaca, N.Y., June 1949, and the American Chemical Society Meeting, San Francisco, Calif., March 1949. The authors were then dispersed to various other laboratories and only in the past year has it been possible to complete the refinement of the structure.

Arsenobenzene was prepared by the reduction of phenylarsonic acid with hypophosphorous acid (Palmer & Scott, 1928). Crystals were obtained by slowly cooling saturated solutions of arsenobenzene in *m*-xylene or chlorobenzene. They were lath shaped, elongated along the *b* axis, about 0.5 mm. long, 0.2 mm. wide and 0.1 mm. thick. The predominant forms were  $\{010\}$ ,  $\{011\}$ ,  $\{100\}$ ,  $\{001\}$  and  $\{10\bar{2}\}$ , in the coordinate system derived from the X-ray analysis. For collection of (*h*0*l*) data a crystal larger than usual was ground into a cylinder about 0.70 mm. long and about 0.30 mm. in diameter, with [010] as cylinder axis.

X-ray photographs were prepared using Cu  $K\alpha$

rays. Sets of oscillation pictures about the three crystallographic axes were used to derive lattice constants, measurements being made on equatorial reflections at high scattering angles. The measurements were corrected for film shrinkage. For intensity measurements multiple film equatorial Weissenberg exposures were prepared about all three axes, and one or more upper layer Weissenbergs were prepared for each axis as a check on the space group assignment. The visually estimated intensities were corrected for the Lorentz-polarization factor and absorption. The latter correction could be made for the (*h*0*l*) data with some assurance because of the cylindrical shape of the crystal. For the (*h**k*0) and (0*k**l*) data, the crystals had a square cross section about  $0.25 \times 0.28$  mm. In applying the absorption correction these were taken to be approximately equivalent to a cylinder of 0.30 mm. diameter, the same as for the (*h*0*l*) data, which has the same cross-sectional area. The observed structure factors, adjusted to the absolute scale of the final calculated values, are shown in Table 1 as  $2.5 \times F$  absolute, rounded to the nearest integer.

The lattice constants found (Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å) are

$$a = 12.16 \pm 0.04, \quad b = 6.22 \pm 0.02, \quad c = 24.10 \pm 0.06 \text{ Å};$$

$$\beta = 110^\circ 14' \pm 5'.$$

The density, measured by flotation in mixtures of ethylene dibromide and carbon tetrachloride at  $26.4^\circ\text{C}$ ., is  $1.81 \pm 0.03$  g.cm.<sup>-3</sup>. With 12  $\text{AsC}_6\text{H}_5$  per cell the calculated density is  $1.77 \pm 0.02$  g.cm.<sup>-3</sup>. Although it is unusual for the observed density to be higher than the X-ray density, the difference does not seem to be significant.

The extinctions observed, *h*0*l* when *l* is odd and 0*k*0 when *k* is odd, indicate the space group  $P2_1/c$ .

### Structure determination

The *h*0*l* Weissenberg photograph has a striking and significant appearance. The strong reflections occur adjacent to each other in groups which are fairly well

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separated from each other by regions containing only moderate to weak reflections. This suggested that there are small, heavily scattering groups which produce a slowly varying absolute contribution to the structure factors. Since the twelve arsenic atoms contain nearly half of the electrons of the cell and the remaining half are scattered over seventy-two carbon atoms and sixty hydrogen atoms, one concludes that the arsenics must be arranged either in relatively small rings about centers of symmetry or in closely coiled chains running up the two-fold screw axes. These positions are widely separated, and the space in between would be occupied by the bulky benzene rings. A Patterson projection on (010) (Fig. 1) confirmed this notion. It proved possible to interpret the diagram in terms of six-membered rings of arsenic atoms centered on centers of symmetry. They are in the chair form, analogous to that of cyclohexane, but with smaller bond angles. The figure shows one such ring superimposed with one atom at the origin; the remaining atoms show the positions of corresponding As-As peaks. By imagining each atom in turn at the origin one can see how, with the aid of the translation operations of the diagram, the entire pattern is explained. It was in fact possible to derive fairly accurate  $x$  and  $z$  parameters for the arsenic atoms from this projection. Patterson projections along [100] and [001] confirmed this arrangement and provided good estimates of the  $y$  coordinates for arsenic atoms. From these results it was clear that the [001] projection would not resolve all arsenic atoms and no further use was made of the ( $hk0$ ) reflections in refining the structure.

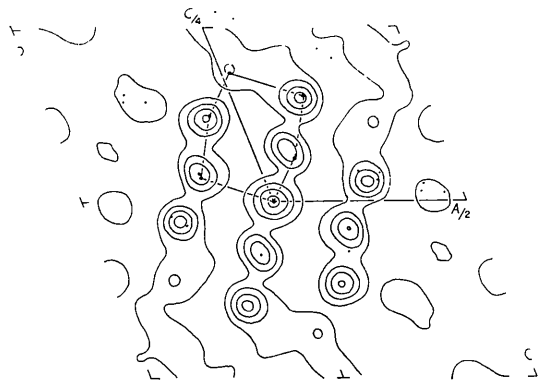


Fig. 1. Patterson projection on (010). Arbitrary contour interval with negative contours omitted. A six-ring of arsenic atoms is shown superimposed with one atom at the origin.

Refinement began by successive Fourier projections along [010] and [100]. In the very first of these the benzene rings appeared. Because of lack of resolution of the carbons and because we were primarily concerned with the arsenic arrangement, it seemed inadvisable to refine separate carbon atoms. Accordingly the carbons were put in so as to form regular,

planar, hexagonal benzene rings with a distance of 1.39 Å between adjacent carbons and with each arsenic to carbon bond lying in the plane of its benzene ring and directed at the center of the ring. Figs. 2 and 3 show the final Fourier projections, each utilizing all but a few of the very small structure factors of the corresponding zone.

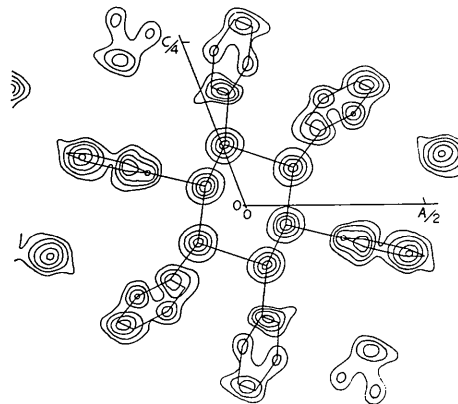


Fig. 2. Fourier projection on (010). Arbitrary contour intervals, zero and first level omitted. For arsenics only every fourth level above the second is shown (i.e., 2nd, 6th, 10th, etc.). The straight lines outline one complete molecule. Portions of neighboring molecules appear.

Final refinement was by least-squares (Hughes, 1941) treatment of the  $h0l$  and  $0kl$  data. The weights used were those proposed by Hughes (1941). Two isotropic temperature factors were included in the refinement, one for arsenics and one for carbons. The carbon parameters were not refined. The scale factor was revised after each refinement. At the very start it was clear that certain large reflections at small scattering angles were seriously affected by extinction. These were given zero weight. Others that later turned out to suffer from some extinction were automatically given very small weight by the weighting system. The  $x$  and  $z$  coordinates were refined first, using only  $h0l$

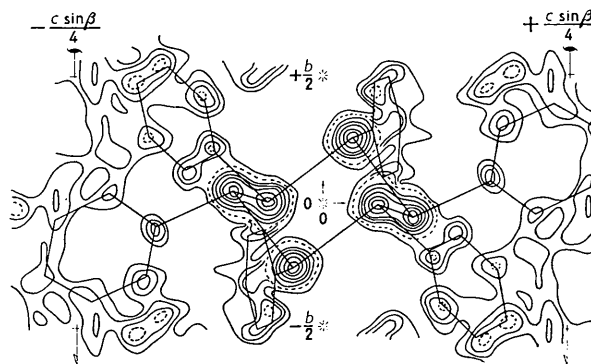


Fig. 3. Fourier projection along [100]. Arbitrary contour interval. Zero and first contour omitted. Fifth contour dashed. Above the fifth only levels divisible by 5 are shown. The straight lines outline one complete molecule. Portions of neighboring molecules appear.

data, and  $y$  coordinates were then refined using the  $0kl$  data with  $z$ 's fixed.

The scattering factors for carbon were those of Berghuis *et al.* (1955). For arsenic, the factors given by Hoerni & Ibers (1954) were corrected for anomalous dispersion by subtracting 1.2 units, as suggested by Dauben & Templeton (1955). The imaginary part of the correction was ignored since there are practically no instances where a large real arsenic contribution is almost balanced out by the carbon contributions. As pointed out by Templeton (1955), this is the only case where the residual imaginary term can cause small reflections to appear significantly larger than the real structure factor would suggest.

Table 2. *Parameters*

	$x$	$y$	$z$
As <sub>1</sub>	+0.0063	-0.0561	+0.0910
As <sub>2</sub>	+0.1713	-0.0095	+0.0554
As <sub>3</sub>	+0.0906	-0.2515	-0.0296
C <sub>4</sub>	+0.073	+0.081	+0.171
C <sub>5</sub>	+0.034	+0.285	+0.180
C <sub>6</sub>	+0.081	+0.384	+0.235
C <sub>7</sub>	+0.167	+0.279	+0.281
C <sub>8</sub>	+0.206	+0.075	+0.272
C <sub>9</sub>	+0.159	-0.024	+0.217
C <sub>10</sub>	+0.283	-0.199	+0.109
C <sub>11</sub>	+0.249	-0.405	+0.120
C <sub>12</sub>	+0.331	-0.542	+0.160
C <sub>13</sub>	+0.447	-0.473	+0.189
C <sub>14</sub>	+0.481	-0.267	+0.178
C <sub>15</sub>	+0.399	-0.130	+0.138
C <sub>16</sub>	+0.232	-0.283	-0.051
C <sub>17</sub>	+0.281	-0.485	-0.052
C <sub>18</sub>	+0.382	-0.505	-0.067
C <sub>19</sub>	+0.434	-0.323	-0.081
C <sub>20</sub>	+0.385	-0.121	-0.080
C <sub>21</sub>	+0.284	-0.101	-0.065

Variances and covariances of As parameters

$$\begin{aligned}\sigma^2(x) &= 13 \times 10^{-8} \\ \sigma^2(z) &= 3.3 \times 10^{-8} \\ \text{cov}(x, z) &= 2.2 \times 10^{-8} \\ \sigma^2(y) &= 1.2 \times 10^{-6}\end{aligned}$$

Standard deviations of As positions

$$\begin{aligned}p(\mathbf{a}^*) &= \sigma(x)/a^* = 4.1 \times 10^{-3} \text{ \AA} \\ p(\mathbf{c}^*) &= \sigma(z)/c^* = 4.1 \times 10^{-3} \\ p(\mathbf{b}) &= \sigma(y)/b = 6.9 \times 10^{-3}\end{aligned}$$

Temperature parameters

$$\begin{aligned}B_{\text{As}} &= 3.8 \text{ \AA}^2 \\ B_{\text{C}} &= 6.0\end{aligned}$$

The errors in the observed structure factors were estimated by comparing them with the calculated structure factors (see Table 1, which includes also values for  $hk0$  reflections). From the weighted sum of the residuals the standard deviations of the arsenic parameters were calculated in the usual way.

The final temperature factors, parameters, and standard deviations are recorded in Table 2.

### Extinction corrections

After the final refinement the actual extent of the

extinction was estimated by considering the calculated intensities to be reasonable approximations of the actual unextinguished values. Only secondary extinction was considered. If  $\mu$  is the ordinary linear absorption coefficient, then it is known (Darwin, 1922) that the effect of secondary extinction is that to be expected if  $\mu$  were to be replaced by a fictitious coefficient  $\mu'$ , given by

$$\mu' = \mu + g_1 Q + g_2 Q^2 + \dots,$$

where  $Q$  is the unextinguished intensity and  $g_1$  and  $g_2$  are constants. We approximate  $Q$  by  $kF_c^2$ , where  $k$  is the Lorentz-polarization factor. Multiplying this equation by the radius  $r$  of the cylindrical sample yields

$$\mu'r = \mu r + g_1 r Q + g_2 r Q^2 + \dots$$

The experimental data had already been corrected for normal absorption corresponding to  $\mu r = 1.10$ , using the tables in the *Internationale Tabellen* (1935). The values of  $\mu'r$  were now estimated for likely reflections by looking in plots of the same tabulated data to see what value of  $\mu'r$  would be required to make  $F_o^2$  equal to  $F_c^2$ . The values of  $\mu'r$  so obtained were plotted against corresponding  $Q$ 's. In fitting the above equation to this plot, it was found necessary to revise slightly the value of  $\mu r$ , from 1.10 to 1.14. This is not surprising since our value of  $r$  was an arithmetic average of two  $r$ 's measured at the top and bottom of the cylindrical sample and  $\mu$  was a calculated value (*Internationale Tabellen*, 1935). The values of  $\mu r$ ,  $g_1 r$  and  $g_2 r$  found in this way, using about two dozen plotted points, were then used with the equation above to compute first  $\mu'r$  and then, from the tables, corrected  $F_o$  values for all reflections that had a correction on  $F$  greater than 6%. Corrections smaller than 6% are probably less than the standard deviations of the observations.

There were six  $0kl$  reflections (with  $k$  different from zero) with corrections ranging from 8 to 28%. The extinction correction caused their  $R$  to drop from 0.107 to 0.050. For the entire zone ( $k \neq 0$ )  $R$  dropped from 0.111 to 0.100. For the entire  $h0l$  zone there were sixteen reflections with corrections ranging from 7 to 50%. Correcting these caused their  $R$  to drop from 0.181 to 0.055 and caused  $R$  for the zone to drop from 0.136 to 0.110. Considering only reflections with large corrections, there were ten from both zones with corrections greater than 14% and applying the corrections caused their  $R$  to drop from 0.234 to 0.066. No extinction corrections were applied to the less reliable  $hk0$  data. They had  $R = 0.150$ . In all of the above

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|},$$

not including unobserved reflections except when the calculated value exceeded the maximum possible observed value. For some few reflections, the extinction corrections actually made the agreement worse; they are included in the  $R$  calculations given above.

If  $Q$  is given in absolute units, using the equation  $Q = [(1 + \cos^2 2\theta)/2 \sin^2 \theta] \cdot (Ne^2/mc^2)^2 \lambda^3 \cdot F^2$ , the values found as described above become:  $\mu = 77.0 \text{ (cm.)}^{-1}$ ,  $g_1 = 1.18 \times 10^3$  and  $g_2 = -1.01 \times 10^4 \text{ cm.}$  (using  $2r = 0.030 \text{ cm.}$ , the average value for the cylinder). The theory predicts that  $g_2$  should be negative. In principle the new value of  $\mu$  should be used to re-correct all data for absorption. But the difference is small and the corrections would be only a fraction of the standard deviation of the observations. Actually some of this error has probably been taken up by the scale factor and temperature factor adjustments.

### Description of the structure

The molecule of  $(\text{AsC}_6\text{H}_5)_6$  is shown in Fig. 4 as it appears looking in the positive direction along the  $b$  axis. There is a center of symmetry at the center, which is the origin of the cell. The underscored numbers adjacent to the arsenic atoms give their heights in Ångström units above the origin (i.e., these are the negatives of their  $y$  coordinates). Atoms designated with primed numbers are related by the center of symmetry to the atoms with corresponding unprimed numbers. Interatomic distances in Ångströms are given for one-half of the molecule and interbond angles are indicated for the other half. Dashed lines indicate non-bonded distances. For distances to neighboring molecules, the neighbors are indicated by letters.

$B$  is the original molecule translated one repeat along  $a$ .  $C$  is the original molecule reflected in the glide plane and translated by  $c/2$ ; it is centered at  $0, \frac{1}{2}, \frac{1}{2}$ .  $D$  is obtained in the same way from  $B$ ; it is centered at  $1, \frac{1}{2}, \frac{1}{2}$ . Primes on the letters indicate an additional translation of  $\pm b$ . Dimensions and angles inside a given benzene ring are not shown since they were all arbitrarily introduced as described above. The intramolecular distances and angles are summarized in Table 3, which also gives some standard deviations.

The three As-As distances are almost identical. The mean value  $2.456 \text{ Å}$  is slightly larger than the bond-table value,  $2.42$  (Pauling, 1960), and differs by almost the same amount from the value  $2.428 \text{ Å}$  found by Burns & Waser (1957) in the arsenomethane pentamer. On the other hand it is smaller than  $2.51 \text{ Å}$ , the shorter of the two values found in metallic arsenic, and is close to the value  $2.44 \text{ Å}$  reported (Maxwell, Hendricks & Mosley, 1935) for gaseous  $\text{As}_4$ .

The As-C distances scatter considerably. If one considers that they should be equal and takes the standard deviation from their mean value, one obtains  $1.966 \pm 0.021 \text{ Å}$ , the standard deviation for a single measurement being  $\pm 0.037 \text{ Å}$ . Since the standard deviation of the arsenic positions is negligibly small compared to the latter value, it must represent approximately the uncertainty in carbon positions. Thus the non-bonded C-C distances probably have a standard deviation of about  $\pm 0.05 \text{ Å}$ . The average As-C

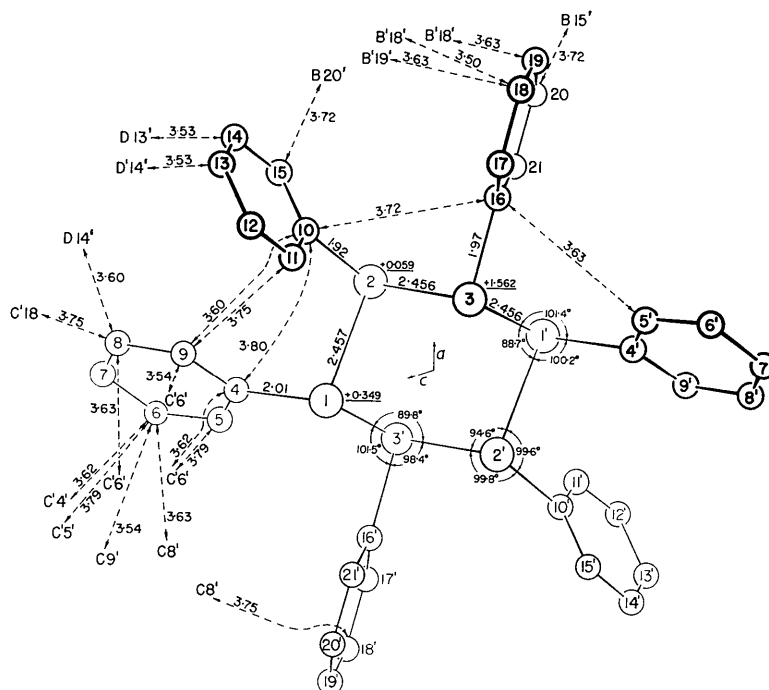


Fig. 4. The molecule viewed along the  $b$ -axis. Large circles are arsenics, small circles carbons. Underscored numbers on arsenics are heights in Ångströms above the plane of the drawing (i.e., negatives of  $y$  coordinates). There is a center of symmetry at the origin of coordinates. Solid lines represent chemical bonds; dashed lines represent van der Waals approaches; distances greater than  $3.80 \text{ Å}$  are not shown. For the system of identifying neighboring molecules see text.

Table 3. Distances and angles in the molecule of arsenobenzene

Distances (bonded)			
As <sub>1</sub> -As <sub>2</sub>	2.457 ± 0.006 Å	As <sub>1</sub> -C <sub>4</sub>	2.01 Å
As <sub>2</sub> -As <sub>3</sub>	2.456 ± 0.008	As <sub>2</sub> -C <sub>10</sub>	1.92
As <sub>3</sub> -As <sub>1</sub>	2.456 ± 0.009	As <sub>3</sub> -C <sub>16</sub>	1.97
Average	2.456 ± 0.005 Å	Average	1.966 ± 0.021 Å
Distances (non-bonded, less than 4.00 Å)			
C <sub>4</sub> -C <sub>10</sub>	3.80 Å	C <sub>10</sub> -C <sub>16</sub>	3.72 Å
C <sub>9</sub> -C <sub>10</sub>	3.60	C <sub>16</sub> -C <sub>5</sub>	3.63
C <sub>9</sub> -C <sub>11</sub>	3.75		
Angles			
As <sub>3</sub> '-As <sub>1</sub> -As <sub>2</sub>	88.7° ± 0.3°	As <sub>3</sub> '-As <sub>1</sub> -C <sub>4</sub>	101.4°
As <sub>1</sub> -As <sub>2</sub> -As <sub>3</sub>	94.6 ± 0.3	As <sub>2</sub> -As <sub>1</sub> -C <sub>4</sub>	100.2
As <sub>2</sub> -As <sub>3</sub> -As <sub>1</sub>	89.8 ± 0.3	As <sub>1</sub> -As <sub>2</sub> -C <sub>10</sub>	99.6
Average	91.0°	As <sub>3</sub> -As <sub>2</sub> -C <sub>10</sub>	99.8
		As <sub>2</sub> -As <sub>3</sub> -C <sub>16</sub>	98.4
		As <sub>1</sub> -As <sub>3</sub> -C <sub>16</sub>	101.5
		Average	100.1°

distance itself is not significantly different from the value 1.95 Å found in arsenomethane nor the radius-able sum of 1.99 Å.

Unlike the distances, the As-As-As bond angles all differ from their mean value, 91.0°, by significant amounts. The packing of the large molecules against each other is so complex that it appears hopeless to find any reason for the bond angle deviations. On the other hand the As-As-C angles are much more nearly the same and certainly do not deviate significantly from their mean value, 100.1°. No attention was paid to these angles in inserting the benzene rings so the value has some experimental significance. In arsenomethane the corresponding mean value is 96.9°, with considerable deviation (94.4 to 102.8°). One would expect that, as found, this angle is larger in arsenobenzene because of repulsion between the benzene rings, which are bulkier than methyl groups. The As-As-As angles of the pentagon in arsenomethane are not to be compared with those in arsenobenzene. The former are certainly strained, and they vary from 97.5 to 105.6° with a mean of 101.8°.

It is not obvious why arsenomethane crystallizes as a pentamer while arsenobenzene crystallizes as a hexamer. Nor is there any completely convincing explanation for the fact that the As-As distances seem significantly larger in the hexamer. The repulsions between the phenyl groups, cited above to explain the larger As-As-C angles, might tend to stretch the As-As bonds some. Also, in the hexamer, where the As-As-As angles are not strained as in the pentamer, next nearest neighbors in the ring become closer, resulting in slightly larger across-ring repulsions. In arsenomethane these distances range from 3.66 to 3.87 Å, with a mean value of 3.77 Å. In arsenobenzene there are two of 3.45 Å and one of 3.61 Å, with a mean of only 3.50 Å.

With only minor changes in bond lengths and angles, and by small rotations of four and moderate rotations of two benzene rings about their bonds to arsenic atoms, the molecule could be made to have the rather high symmetry of  $\bar{3}2/m$  instead of only  $\bar{1}$ .

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