

569. *Molecular Polarisability. The Conformations of Certain Di-ortho-substituted Phenols and Anisoles.*

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Polarisability ellipsoid specifications and thence molar Kerr constants are calculated, from bond and group polarity and polarisability data, for various conformations of certain 2,4,6-trisubstituted phenols and anisoles. Comparison with values observed in benzene solution, leads to the following conclusions: (a) 2,4,6-tribromophenol and 2,4,6-tri-*t*-butylphenol have near-planar structures (the angle, ϕ , between the $C_{Ar}-O-H$ plane and that of the benzene ring, is *ca.* 12° and *ca.* 14° , respectively); (b) the introduction of methyl, chloro-, or bromo-substituents in both *ortho*-positions of anisole results in conformations having the $C_{Ar}-O-C_{Me}$ plane orthogonal with the aromatic ring.

IN this Paper, the molecular configurations of certain *ortho*-substituted phenols and anisoles, examined as solutes in benzene, are deduced by comparing the observed molar Kerr constants with those theoretically predictable for various possible conformations. Observations and results are summarised under usual ^{1,2} headings in Tables 1 and 2.

¹ Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

² Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, 5, 261; (b) *J.*, 1953, 4041; (c) *J.*, 1954, 1577; (d) "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York and London, 3rd edn., vol. 1, ch. XXXVI, p. 2459.

TABLE 1.

Incremental Kerr effects, refractive indices, dielectric constants, and densities for solutions in benzene at 25°.

| | | | | | | | | | | | | |
|---|---------|---------|--------|---------|--------|---|----------------|---------|---------|---------|---------|---------|
| <i>Solute: 2,4,6-Tribromophenol</i> | | | | | | | | | | | | |
| $10^5 w_2$... | 4114 | 5101 | 5144 | 6159 | 7171 | $10^5 w_2$... | 3760 | 4914 | 5920 | 7433 | 7788 | |
| $10^7 \Delta B$... | 0.095 | 0.120 | 0.123 | 0.151 | 0.177 | d_4^{25} | 0.8953 | 0.9018 | 0.9082 | 0.9169 | 0.9189 | |
| whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 2.41$. | | | | | | whence $\Sigma \Delta d / \Sigma w_2 = 0.577$. | | | | | | |
| <i>Solute: 2,4,6-Tri-t-butylphenol</i> | | | | | | | | | | | | |
| $10^5 w_2$... | 2747 | 5535 | 5631 | 8184 | 9462 | 10,485 | $10^5 w_2$... | 4379 | 4437 | 5535 | 8184 | 9148 |
| $10^7 \Delta B$... | 0.029 | 0.057 | 0.059 | 0.089 | 0.104 | 0.113 | d_4^{25} ... | 0.87520 | 0.87524 | 0.87551 | 0.87627 | 0.87671 |
| whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 1.07$. | | | | | | whence $\Sigma \Delta d / \Sigma w_2 = 0.032$. | | | | | | |
| <i>Solute: 2,4,6-Trimethylanisole</i> | | | | | | | | | | | | |
| $10^5 w_2$ | 3573 | 4563 | 5163 | 5787 | 7795 | 8612 | 9838 | 18,222 | | | | |
| $10^7 \Delta B$ | -0.101 | -0.129 | -0.154 | -0.160 | -0.222 | -0.247 | — | — | | | | |
| ϵ^{25} | 2.3153 | 2.3265 | 2.3341 | 2.3423 | 2.3671 | 2.3783 | — | — | | | | |
| d_4^{25} | 0.87577 | 0.87633 | — | 0.87706 | — | — | 0.87911 | 0.88385 | | | | |
| whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -2.85$; $\Sigma \Delta \epsilon / \Sigma w_2 = 1.21$; $\Sigma \Delta d / \Sigma w_2 = 0.055$. | | | | | | | | | | | | |
| <i>Solute: 2,4,6-Trichloroanisole</i> | | | | | | | | | | | | |
| $10^5 w_2$ | 2828 | 3485 | 3931 | 4457 | 5618 | 6923 | | | | | | |
| $10^7 \Delta B$ | -0.105 | -0.131 | -0.156 | -0.163 | -0.219 | -0.275 | | | | | | |
| $10^4 \Delta n$ | 9 | 11 | 13 | 15 | 19 | 23 | | | | | | |
| ϵ^{25} | 2.3057 | 2.3119 | 2.3172 | 2.3230 | 2.3373 | 2.3539 | | | | | | |
| d_4^{25} | 0.8833 | 0.8857 | 0.8873 | 0.8887 | 0.8930 | 0.8976 | | | | | | |
| whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -3.85$; $\Sigma \Delta n / \Sigma w_2 = 0.034$; $\Sigma \Delta \epsilon / \Sigma w_2 = 1.15$; $\Sigma \Delta d / \Sigma w_2 = 0.341$. | | | | | | | | | | | | |
| <i>Solute: 2,4,6-Tribromoanisole</i> | | | | | | | | | | | | |
| $10^5 w_2$ | 1978 | 2738 | 2987 | 4345 | 4455 | 4771 | 6892 | | | | | |
| $10^7 \Delta B$ | -0.047 | -0.066 | -0.072 | -0.109 | -0.109 | -0.111 | -0.167 | | | | | |
| ϵ^{25} | 2.2881 | 2.2943 | — | — | 2.3081 | — | 2.3276 | | | | | |
| whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -2.42$; $\Sigma \Delta \epsilon / \Sigma w_2 = 0.80$. | | | | | | | | | | | | |
| <i>Solute: 2,4,6-Tribromoanisole</i> | | | | | | | | | | | | |
| $10^5 w_2$ | 2696 | 3231 | 4076 | 5883 | 6767 | 7903 | | | | | | |
| $10^4 \Delta n$ | 14 | 17 | 21 | 30 | 35 | 41 | | | | | | |
| d_4^{25} | 0.8881 | 0.8913 | 0.8957 | 0.9058 | 0.9106 | 0.9169 | | | | | | |
| whence $\Sigma \Delta n / \Sigma w_2 = 0.052$; $\Sigma \Delta d / \Sigma w_2 = 0.542$. | | | | | | | | | | | | |

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions in benzene at 25°).

| Solute | $\alpha \epsilon_1$ | β | γ | δ | ∞P_2 (c.c.) | R_D (c.c.) | μ (D) | 10^{12} $\infty (mK_2)$ |
|-----------------------------|---------------------|---------|----------|----------|------------------------|-----------------|-----------|------------------------------|
| 2,4,6-Tribromophenol ... | 0.97 * | 0.660 | 0.040 * | 5.88 | — | — | 1.55 * | 142 |
| 2,4,6-Tri-t-butylphenol ... | 1.10 * | 0.037 | -0.003 * | 2.61 | — | — | 1.63 * | 60.6 |
| 2,4,6-Trimethylanisole ... | 1.21 | 0.063 | ca. 0 | -6.95 | 82.2 | 47.2 | 1.26 † | -72.9 |
| 2,4,6-Trichloroanisole ... | 1.15 | 0.390 | 0.023 | -9.39 | 89.7 | 47.4 | 1.40 † | -149 |
| 2,4,6-Tribromoanisole ... | 0.80 | 0.620 | 0.035 | -5.90 | 96.4 | 54.1 | 1.39 † | -156 |

* From Goode and Ibbitson, *J.*, 1960, 4265. † Calculated assuming $D^P = 1.05R_D$.

EXPERIMENTAL

Materials, apparatus, etc.—The solutes were prepared and/or purified immediately before use, to give: 2,4,6-tribromophenol, m. p. 94°; 2,4,6-tri-t-butylphenol, m. p. 131°; 2,4,6-trimethylanisole, b. p. 90–92°/ca. 20 mm.; 2,4,6-trichloroanisole, m. p. 61°; 2,4,6-tribromoanisole, m. p. 87°. Apparatus, techniques, symbols used, and methods of calculation have been described before.^{1,2} The quantities $\Delta \epsilon$, Δd , Δn , and ΔB are the differences found between the dielectric constants, densities, refractive indexes, and Kerr constants, respectively, of benzene as solvent and of solutions containing weight fractions w_2 of solute. The following data apply at 25° to benzene: $\epsilon_1 = 2.2725$; $d_1 = 0.87378$; $(n_1)_D = 1.4973$; $10^7 B_1 = 0.410$; $10^{12} K_1 = 0.0756$.

Previous Measurements.—The following dipole moments (μ) have been recorded: 2,4,6-tribromophenol, 1.56 (in C_6H_6);³ 1.55 (in C_6H_6);⁴ 1.44 (in cyclohexane);⁵ 1.98 (in dioxan);⁵ 2,4,6-tri-*t*-butylphenol, 1.63 (in C_6H_6);⁴ 1.55 (in cyclohexane);⁵ 1.57 (in dioxan);⁵ 2,4,6-trimethylanisole, 1.27 (in C_6H_6).⁶

DISCUSSION

*2,4,6-Tribromophenol and 2,4,6-Tri-*t*-butylphenol.*—Goode and Ibbitson⁴ have shown that the dipole moments of symmetrically trisubstituted phenols are not much affected by the size of the substituent groups (*e.g.*, as μ units they are 1.54, 1.55, and 1.63 for $X = H, Br,$ and But , respectively, in $C_6H_2X_3OH$) and cannot be used to estimate, with any degree of certainty, the extent to which the oxygen-bonded proton can be forced out of the benzene-ring plane. By theory the molar Kerr constants of these compounds should be sensitively dependent, both in magnitude and in algebraic sign, on the disposition of the molecular dipole moment relative to the benzene-ring plane. Accordingly, we have calculated, by addition of the component bond and group parameters, the polarisability ellipsoid specifications, and thence the corresponding expected molar Kerr constants, for various possible conformations of these molecules. The computational procedures are outlined in ref. 2*d*, pp. 2483—2486. Bond and group polarisability semi-axes * used in the subsequent calculations are:

| | b_L | b_T | b_V | Ref. |
|---------------------------------------|---------|---------|---------|------------|
| C-H | 0.064 | 0.064 | 0.064 | 2 <i>a</i> |
| C-C | 0.099 | 0.027 | 0.027 | 7 |
| C-O | 0.081 † | 0.039 † | 0.039 † | 7 |
| O-H | 0.095 | 0.050 | 0.050 | 8 |
| Phenyl..... | 1.056 | 1.056 | 0.672 | 9 |
| 2,4,6-Tribromophenyl | 2.098 | 2.098 | 1.247 | See text |
| 2,4,6-Tri- <i>t</i> -butylphenyl..... | 3.204 | 3.204 | 2.820 | „ „ |

† Present calculations had been carried out prior to the redetermination of the C-O bond semi-axes by Le Fèvre, Sundaram, and Pierens.¹⁰ The revised estimates yield a slightly smaller b_L/b_T ratio but our conclusions are not affected by this.

Le Fèvre *et al.*¹¹ have recorded the $\infty(mK_2)$ for 1,3,5-tribromobenzene as 34.8×10^{-12} , the distortion polarisation as 50.1 c.c., and the electronic polarisation as 47.4 c.c., from which can be calculated, using equations (1) and (2), the anisotropic polarisabilities of this molecule ($b_1 = b_2 = 2.162$; $b_3 = 1.311$). Subtraction of one C-H bond equivalent from each yields the 2,4,6-tribromophenyl-group polarisability specifications. The semi-axes of the 2,4,6-tri-*t*-butylphenyl group are derived by addition of the appropriate number of C-C and C-H bond polarisabilities to the phenyl group semi-axes.

$${}_mK = 4\pi N_D P (b_1 - b_3)^2 / 405 k T_E P \quad (1)$$

$${}_E P = 4\pi N (2b_1 + b_3) / 9 \quad (2)$$

Fig. 1*a* represents a structure in which the $C_{Ar}-O-H$ group ($R = H$ for the phenols) is in the plane of the benzene ring (the XY plane), and this conformation we define by $\phi = 0^\circ$. Fig. 1*b* is generated from 1*a* by rotating the $C_{Ar}-O-H$ group, about the $C_{Ar}-O$ bond as axis, through 90° (*i.e.*, $\phi = 90^\circ$). The C-O-R bond angles are assumed to be 110° . The calculations are summarised in Table 3; the principal axes are located within the

* Polarisability semi-axes of bonds or groups, b_L , b_T , and b_V , or of molecules, b_1 , b_2 , and b_3 , are quoted throughout in 10^{-23} c.c. units.

³ Hassel and Naeshagen, *Z. phy. Chem.*, 1931, *B*, **12**, 79.

⁴ Goode and Ibbitson, *J.*, 1960, 4265.

⁵ Eric, Goode, and Ibbitson, *J.*, 1960, 55.

⁶ Lumbroso and Dumas, *Bull. Soc. chim. France*, 1955, 651.

⁷ Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

⁸ Le Fèvre, Le Fèvre, Purnachandra Rao, and Williams, *J.*, 1960, 123.

⁹ Aroney and Le Fèvre, *J.*, 1960, 3600.

¹⁰ Le Fèvre, Sundaram, and Pierens, *J.*, 1963, 479.

¹¹ Le Fèvre *et al.*, unpublished work.

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co-ordinate system X , Y , and Z , in Fig. 1. We have not attempted to take into account polarisability exaltations arising from delocalisation of the oxygen lone-pair electrons; most likely these are very small [cf., Le Fèvre and Williams,¹² who have shown for five-*para*-substituted phenols that $\Sigma b_i(\text{obs.}) \approx \Sigma b_i$ (calculated assuming no interaction of the

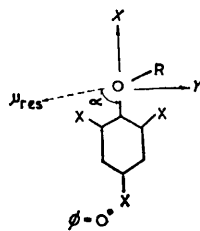


FIG. 1a.

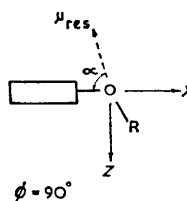


FIG. 1b.

hydroxyl group with the *para*-substituent]). Following Goode and Ibbitson's conclusions⁴ for phenol, we assume that the observed dipole moment in each case is located in the plane $C_{Ar}-O-H$ such that it makes an angle of 88° with the $C_{Ar}-O$ bond ($\alpha = 88^\circ$ in Fig. 1). The observed molar Kerr constants are $+142 \times 10^{-12}$ (for 2,4,6-tribromophenol) and $+60.6$

TABLE 3.
Calculated polarisability semi-axes and molar Kerr constants

| Solute | ϕ° | b_i (calc.) | Direction cosines with | | | $10^{12} mK$ (calc.) |
|----------------------------------|--------------|---------------|------------------------|--------|---------------------|-------------------------|
| | | | X | Y | Z | |
| 2,4,6-Tribromophenol | 0 | $b_1 = 2.245$ | +0.786 | +0.619 | 0 | +156 |
| | | $b_2 = 2.216$ | -0.619 | +0.786 | 0 | |
| | | $b_3 = 1.336$ | 0 | 0 | +1 | |
| ,, | 13 | $b_1 = 2.244$ | +0.812 | +0.583 | +0.009 | +140 |
| | | $b_2 = 2.215$ | -0.583 | +0.812 | +0.006 | |
| | | $b_3 = 1.338$ | -0.004 | -0.010 | +0.999 ₉ | |
| ,, | 90 | $b_1 = 2.234$ | +0.999 ₉ | 0 | +0.017 | -187 |
| | | $b_2 = 2.187$ | 0 | +1 | 0 | |
| | | $b_3 = 1.376$ | -0.017 | 0 | +0.999 ₉ | |
| 2,4,6-Tri- <i>t</i> -butylphenol | 0 | $b_1 = 3.351$ | +0.786 | +0.619 | 0 | +71 |
| | | $b_2 = 3.322$ | -0.619 | +0.786 | 0 | |
| | | $b_3 = 2.909$ | 0 | 0 | +1 | |
| ,, | 15 | $b_1 = 3.350$ | +0.813 | +0.582 | +0.020 | +59 |
| | | $b_2 = 3.320$ | -0.582 | +0.813 | +0.015 | |
| | | $b_3 = 2.911$ | -0.008 | -0.024 | +0.999 ₇ | |
| ,, | 90 | $b_1 = 3.341$ | +0.999 | 0 | +0.037 | -101 |
| | | $b_2 = 3.293$ | 0 | +1 | 0 | |
| | | $b_3 = 2.948$ | -0.037 | 0 | +0.999 | |

(for 2,4,6-tri-*t*-butylphenol), from which we infer that ϕ is *ca.* 12° and *ca.* 14° , respectively. Leybold models indicate that near-planar forms such as these are sterically allowable.

Anisole, and Certain 2,4,6-Trisubstituted Anisoles.—Aroney, Le Fèvre, and Shu-Sing Chang¹³ had earlier recorded the dipole moment and molar Kerr constant of anisole, in carbon tetrachloride solution, as 1.24_5 D and $+28.8 \times 10^{-12}$, respectively, from which data they concluded that "the $C_{Ar}-O-Me$ triangle is twisted 18° out of the C_6 -plane." In the present work we redetermined the theoretical molar Kerr constant as a function of the angle ϕ , using (a) a more sophisticated method of computing the polarisability specifications for a particular molecular model, and (b) the correct location of μ_{res} , as given by Lumbroso and Dumas in ref. 6 (*i.e.*, corresponding to $\alpha = 76^\circ$ in Fig. 1a); for the earlier work (cf., ref. 13) α had been incorrectly quoted as 104° . We find now that mK (calc.) agrees with the experimental value for $\phi = 22^\circ$.

In the cases of the 2,4,6-trisubstituted anisoles ($C_6H_2X_3OMe$, where $X = Me, Cl$, and Br), molecular polarisability semi-axes and molar Kerr constants have been calculated for

¹² Le Fèvre and Williams, *J.*, 1960, 1825.

¹³ Aroney, Le Fèvre, and Shu-Sing Chang, *J.*, 1960, 3173.

conformations defined by $\phi = 0$ and $\phi = 90^\circ$ (Table 4). For the 2,4,6-trichlorophenyl group, $b_L = b_T = 1.768$, $b_V = 0.943$ (ref. 11), and for the 2,4,6-trimethylphenyl group, $b_L = b_T = 1.624$, $b_V = 1.174$ (ref. 14). In calculating the molar Kerr constants of Table 4 we have assumed that the resultant dipole moment acts in each case at 90° to the $C_{Ar}-O$

TABLE 4.
Calculated polarisability semi-axes and molar Kerr constants.

| Solute | ϕ | b_i (calc.) | Direction cosines with | | | $10^{12} \mu_m K$ (calc.) |
|------------------------|--------|--|--|--|--|------------------------------|
| | | | X | Y | Z | |
| 2,4,6-Trimethylanisole | 0 | $\left\{ \begin{array}{l} b_1 = 1.950 \\ b_2 = 1.922 \\ b_3 = 1.444 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.819 \\ -0.574 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.574 \\ +0.819 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} 0 \\ 0 \\ +1 \end{array} \right.$ | +53 |
| | 90 | $\left\{ \begin{array}{l} b_1 = 1.941 \\ b_2 = 1.894 \\ b_3 = 1.481 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.999_6 \\ 0 \\ -0.029 \end{array} \right.$ | $\left\{ \begin{array}{l} 0 \\ +1 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.029 \\ 0 \\ +0.999_6 \end{array} \right.$ | |
| 2,4,6-Trichloroanisole | 0 | $\left\{ \begin{array}{l} b_1 = 2.094 \\ b_2 = 2.066 \\ b_3 = 1.213 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.819 \\ -0.574 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.574 \\ +0.819 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} 0 \\ 0 \\ +1 \end{array} \right.$ | +128 |
| | 90 | $\left\{ \begin{array}{l} b_1 = 2.085 \\ b_2 = 2.038 \\ b_3 = 1.250 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.999_9 \\ 0 \\ -0.016 \end{array} \right.$ | $\left\{ \begin{array}{l} 0 \\ +1 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.016 \\ 0 \\ +0.999_9 \end{array} \right.$ | |
| 2,4,6-Tribromoanisole | 0 | $\left\{ \begin{array}{l} b_1 = 2.424 \\ b_2 = 2.396 \\ b_3 = 1.517 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.819 \\ -0.574 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.574 \\ +0.819 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} 0 \\ 0 \\ +1 \end{array} \right.$ | +132 |
| | 90 | $\left\{ \begin{array}{l} b_1 = 2.415 \\ b_2 = 2.368 \\ b_3 = 1.554 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.999_9 \\ 0 \\ -0.016 \end{array} \right.$ | $\left\{ \begin{array}{l} 0 \\ +1 \\ 0 \end{array} \right.$ | $\left\{ \begin{array}{l} +0.016 \\ 0 \\ +0.999_9 \end{array} \right.$ | |

bond ($\alpha = 90^\circ$ in Fig. 1a and 1b). The values so obtained for $\phi = 90^\circ$ (*i.e.*, for conformations in which the $C_{Ar}-O-Me$ group is orthogonal with the benzene-ring plane) agree reasonably with the $\infty(mK_2)$'s of Table 2: -72.9×10^{-12} (2,4,6-trimethylanisole), -149×10^{-12} (2,4,6-trichloroanisole), and -156×10^{-12} (2,4,6-tribromoanisole). It should be noted that accord between experiment and calculation can be achieved only if both ϕ and α are equal to or are very close to 90° .

The Three Dimethoxybenzenes.—Aroney, Le Fèvre, and Shu-Sing Chang¹³ have shown that for each of the dimethoxybenzenes, studied as solutes in carbon tetrachloride, no single conformation can be found for which the calculated dipole moment and molar Kerr constant both agree with the observed quantities. They postulate the existence in solution of mixtures of rotational isomers [see Figs. (IIa—d), (IIIa—f), and (IVa—h) of ref. 13]. We have re-examined this problem using (a) the computational method set out in refs. 2d and 15, and (b) the corrected location of the methoxy-group moment as given earlier for anisole. Our conclusions do not differ much from those of ref. 13. If each methoxy-group of *m*-dimethoxybenzene is effectively located 22° out of the benzene-ring plane (as for anisole), then six rotational isomers are predicted [see Figs. (IIIa—f) of ref. 13], in which *t* and *u* now indicate 22° up and 22° down, respectively. A mixture in which all six forms participate, with (IIIe) and (IIIf) (which are sterically the least favoured) contributing to a smaller degree than the others, appears most likely and is reconcilable with the measurements. With *p*-dimethoxybenzene, which has two electron-donor groups *para* to one another, agreement can be achieved between the calculated and experimental values if the solute is regarded as an equimolecular mixture of isomers in which each methoxy-group is effectively located 32° above or below the benzene-ring plane. In the case of *o*-dimethoxybenzene, our conclusions are identical with those given in the discussion on pp. 3176—3177 of ref. 13.

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¹⁴ Aroney, Corfield, and Le Fèvre, *J.*, 1964, 648.

¹⁵ Eckert and Le Fèvre, *J.*, 1962, 1081.