# **390.** *The Electric Dipole Moment and Stereochemistry of 2 : 5-Dibromo-1 : 4-di-*tert.*-butylbenzene.*

By Helmer Kofod, Lovraj Kumar, and L. E. Sutton.

2 : 5-Dibromo-1 : 4-di-*tert.*-butylbenzene was suggested by Everard and Sutton (*J.*, 1949, 2312) as a test compound for a hypothesis involving out-of-plane deflection of bulky neighbouring substituent groups on an aromatic ring system. It has been synthesized : its electric dipole moment was found to be less than 0·4 D. and possibly equal to zero. The relation of this result to the hypothesis is discussed.

In order to explain the abnormally high electric dipole moment of 4 : 8-dichloro-1 : 5-dimethoxynaphthalene, which exceeds that of 1 : 5-dimethoxynaphthalene by *ca.* 0·3 D., Everard and Sutton (*J.*, 1949, 2312) suggested that out-of-plane deflection of the bulky neighbouring groups gives rise to structures of which some are non-centrosymmetrical and hence possess a permanent dipole moment. The hypothesis is illustrated in Fig. 1 for the case of 2 : 5-dibromo-1 : 4-di-*tert.*-butylbenzene, which was suggested as a test compound by the above authors.

Fig. 1.

*Scale diagram of 2 : 5-dibromo-1 : 4-di-*tert.*-butylbenzene.*

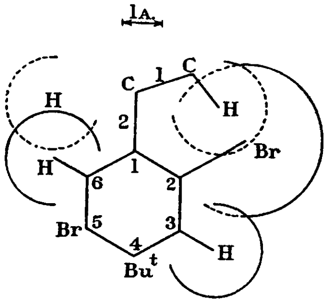


Fig. 3.

*o-Dichlorobenzene.*

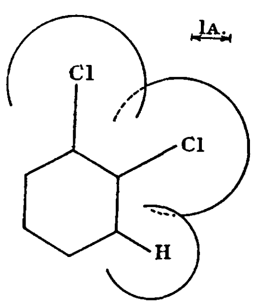
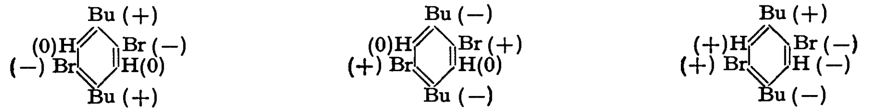


Fig. 2.



(I.) *Polar.* (II.) (III.) *Non-polar.*

(+) *indicates " above ring plane "* ; (−) *indicates " below ring plane."*

Fig. 1 shows the degree of steric interference between a bromine atom and a *tert.*-butyl group in the position of maximum steric interference. The envelope of the *tert.*-butyl group is easily visualized by simultaneous rotation of the hydrogen contour round both the σ-bonds 1 and 2 as axes. The van der Waals radii (H, 1·2 A.; Br, 2·0 A.) and the interatomic distances are those given by Pauling (" Nature of the Chemical Bond," Cornell U.P., 1945). If these dimensions are applicable, and the free rotation about these σ-bonds is maintained, then the steric interference in the molecule is very considerable. The compression cannot be completely relieved by deflection *in* the plane of the ring, involving widening of the valency angle, because of the presence of 3 : 6-hydrogen atoms, but only by some deflection of bonds *out-of-plane*. This is in principle illustrated in Fig. 2. Both the structure (I) and the structure (II), which is the mirror image of (I), lack centrosymmetry and because the moments produced by substitution of the *tert.*-butyl group and the bromine atom into benzene are in opposite directions ($\overset{+\!\!\longrightarrow}{\text{Bu}^{t} - \text{Ph}}$, $\overset{+\!\!\longrightarrow}{\text{Ph} - \text{Br}}$), have a non-zero dipole moment, whereas (III) is centrosymmetrical and has zero moment. Provided that the substance is not wholly of structure III it should have a non-zero average moment.

If free rotation and van der Waals radii be assumed, as above, then it is found from models that a deflection angle of 30° will reduce the van der Waals overlap between the *tert.*-butyl envelope and the bromine to *ca.* 0·5 A.; and this would correspond to an observed moment of 0·7 D. This angle is defined as that between any deflected bond and the ring plane, the deflection being supposed to take place at right angles to the ring plane.

The situation of *minimum* overlap in the molecule is realized when the free rotation round at least the axis 2 (Fig. 1) is stopped and the bromine atom is trapped in between two methyl groups of the *tert.*-butyl group. A model shows the radial overlap of the bromine in this instance to be about 0·5 A. with each of the two interfering hydrogen atoms, one from each of the two methyl groups. The permanent deformation of the molecule in this instance should be small and almost certainly symmetrical. The expected dipole moment would be zero.

It was hoped that the electric dipole moment actually measured for the test compound could throw some light on the steric situation in this molecule, and in the naphthalene derivatives.

2 : 5-Dibromo-1 : 4-di-*tert.*-butylbenzene has been prepared in a pure state and its electric dipole moment measured in benzene solution at 25°. The moment was found to be indistinguishable from zero. The apparent orientation polarisation calculated in the conventional manner as the difference between the total polarisation at radio-frequency and the molecular refraction for the sodium *D* line is 2·7 ± 0·6 cm.$^3$. The significance of this value is uncertain, because the correction for the atom polarisation made by thus taking the refractivity for the sodium *D* line instead of for infinite wave-length is only a partial and purely empirical one. A better correction may possibly be made from the total polarisations of the parent compounds *p*-di-*tert.*-butylbenzene, *p*-dibromobenzene, and benzene. If we assume that these compounds are non-polar (this has been directly demonstrated for benzene from the temperature invariance of the total polarisation) then the total polarisations are made up only of the electron and atom polarisations. By assuming further, as is commonly done, that the electron polarisations are additive (this is true for this series within about 0·7 cm.$^3$; see below) and that the atom polarisation is so too (see below), the total polarisations of the parent compounds *a*, *b*, and *c* (Table I) can be used to predict the sum of the electron and atom polarisations for the test compound *d* from the relation $P_d = P_a + P_b - P_c$. This gives 80·5 ± 0·9. The observed total polarisation is 81·9 ± 0·5, so the orientation polarisation cannot be more than 1·4 ± 1·4 cm.$^3$. The moment, therefore, cannot be greater than 0·4 D., corresponding to ${}_0P = 2{\cdot}8$ cm.$^3$, and is possibly zero. It will be noticed that the values for $[R]_D$ and $[R]_\infty$ obtained by the additivity rule (bottom line of Table I) are somewhat smaller than the observed ones, suggesting that the additive value for ${}_TP$ may be lower than the true sum of the electron and atom polarisations. This would mean that the value ${}_0P$ is about 0—0·7 cm.$^3$, so the moment is between 0 and 0·28 D. These we believe to be the most probable limits.

TABLE I.

*Polarisations and molar refractions at* 25°.

| | *P*. | $[R]_D$. | $[R]_\infty$. |
|---|---|---|---|
| *a*. *p*-Di-*tert.*-butylbenzene | 65·3 ± 0·4 | 63·7 ± 0·1 | 60·6 ± 0·5 |
| *b*. *p*-Dibromobenzene | 41·8 ± 0·5 [1] | 41·0 ± 0·1 [2] | 39·4 ± 0·5 |
| *c*. Benzene | 26·6 | 26·2 | 25·1 |
| *d*. 2 : 5-Dibromo-1 : 4-*tert.*-butylbenzene | 81·9 ± 0·5 | 79·2 ± 0·1 | 76·9 ± 1·0 |
| $P_a + P_b - P_c$ | 80·5 ± 0·9 | 78·5 ± 0·2 | 74·9 ± 1·0 |

*Other values*: [1] 43·8 at 20° (Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425); 40·4 ± 2 at 20° (Walden and Werner, *ibid.*, 1929, *B*, **2**, 10). [2] 42·4 at 20° (Tiganik, *loc. cit.*); 39·7 at 20° (Walden and Werner, *loc. cit.*).

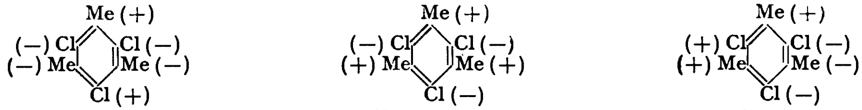
The values recorded in Table I for the compounds *a*, *b*, and *d* are based on our own measurements, exactly the same experimental technique having been applied to all three. For benzene the values have been calculated from standard absolute values of dielectric constant 2·2727 (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664), specific volume 1·14515, and refractive index $n_D^{25}$ 1·49800 (Egloff: "Physical Constants of Hydrocarbons," Vol. 3, p. 26, New York, 1946).

The assumption that atom polarizations are additive needs discussion. The atom polarization or vibration polarization is due to displacements of the atomic nuclei in the molecule, caused by the alternating field applied during the measurements of dielectric constant (cf. Sutton, *Ann. Reports*, 1940, **37**, 57). The resulting periodic distortion may be described as composed of stretching and relative bending of the individual bonds, so the atom polarization includes bond terms and inter-bond terms. Whereas the former are probably additive, the latter may be less perfectly so, because the bending force constants may not be independent of the configuration. It would, however, be reasonable, at least from mechanical analogies, to suppose the freedom of bending vibrations to be less in 2 : 5-di-bromo-1 : 4-di-*tert.*-butylbenzene than in either of the parent compounds. If this be true, then the atom polarization, obtained arithmetically from the polarizations of the parent compounds, will provide a maximum value.

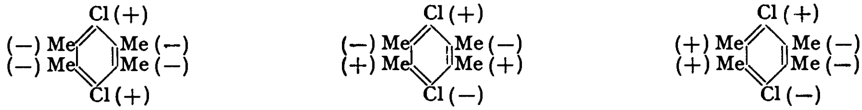
The vanishingly small moment of the substance does not necessarily disprove the out-of-plane deflection hypothesis, which in any case is supported by other evidence. Thus, Bastiansen and Hassel (*Acta Chem. Scand.*, 1947, **1**, 489), by electron-diffraction examination of *o*-dichlorobenzene, found a deflection angle of 18° between the ring plane and one C–Cl bond, the two C–Cl bonds being bent orthogonally to the ring plane and to opposite sides. The same angle was found for *o*-dibromobenzene, although the van der Waals radius of bromine is slightly larger (2·0 A. against 1·8 A.). In both compounds, the steric interference is much less than the maximum in dibromodi-*tert.*-butylbenzene (compare Figs. 1 and 3) if there be free rotation of the butyl groups therein. On these grounds, therefore, we should expect a permanent deflection to occur in the latter compound also, if there is free rotation and if the effective size of groups is at all related to their conventional van der Waals radii. We should thus be led to the conclusion that the centrosymmetric structure (III) (Fig. 2) is favoured much more than the polar ones (I) or (II).

If, however, we suppose that the rotation of the butyl group is stopped, as it could be by a potential barrier of only *ca.* 600 cals./mole, then there would be minimum overlap, and the steric interference would be only of the same order as that in *o*-dichlorobenzene (*ca.* 0·5 A. overlap). Since the bromine atom will overlap with methyl groups on both sides of the benzene ring plane, the σ-bonds attaching the groups to the ring could remain in its plane; and even if they did not, the deflection might not be sufficient to give an average moment outside the limits which we ascribe.

FIG. 4.



*Weakly polar.* *Very polar.* *Polar.*



*Very polar.* (A.) *Non-polar.* (B.) *Non-polar.* (C.)

(+) *indicates " above ring plane "* ; (−) *indicates " below ring plane."*

We cannot claim, therefore, to have proved or disproved the original deflection hypothesis. We can say that if there is such deflection in dibromodi-*tert.*-butylbenzene then the centrosymmetric form (III) is predominant. This is consistent with what is known of the force-constant system of benzene. If the scheme proposed by Bell be applicable (*Trans. Faraday Soc.*, 1945, **41**, 293; cf. Garforth, Ingold, and Poole, *J.*, 1948, 502) then, because of the torsional terms between the adjacent pairs of bonds projecting from the ring, it follows that in the two types of structure (I) or (II) and (III), the carbon–hydrogen bonds at the 4- and 6-positions will respectively stay in the ring plane and tend to be deflected as shown (Fig. 2). It should be noted that, since we are considering static deflections, we have no need to observe the limitations imposed on vibrational modes by the principle of conservation of momentum. The torsional distortion is therefore greater in structures (I) or (II) than in (III): so the strain energy is greater in the former than in the latter.

It seems more probable that free rotation is stopped, and that the bromine atom fits into a " pocket " between two of the methyl groups. This supposition could be tested by examining 4 : 8-dibromo-1 : 5-dimethylnaphthalene, which we hope to do: each methyl group as a whole would be in the position of maximum interference; and although there are " pockets " in it, these are small relative to the bromine atom; so the methyl group may quite well be regarded as axially symmetrical.

It is also a possible conclusion that conventional van der Waals radii are too large for the purpose of such discussions. The following facts, in particular, support this view. Bastiansen and Hassel (*loc. cit.*) found in hexachlorobenzene a deflection angle of 12°. Now, the van der Waals radii of chlorine and of methyl are comparable; so the deflection in dichlorodurene and trichloromesitylene should also be about 12°. In actual fact, both compounds have moments indistinguishable from zero (≯0·25 D. and ≯0·1 D., respectively; Smyth and Lewis, *J. Amer. Chem. Soc.*, 1940, **62**, 721); and it is impossible to account for these observations if the mode of out-of-plane deflection were the same in both compounds. The possibilities are represented in Fig. 4 : it will be seen that no one mode makes both compounds non-polar, although (C) comes near to doing it because it would make dichlorodurene non-polar and would give trichloromesitylene an apparent moment of only $(2{\cdot}1 \sin 12^\circ)/\sqrt{2} = 0{\cdot}31$. In order to maintain that there is out-of-plane deflection in these compounds, therefore, it would be necessary to make *ad hoc* postulates about specific modes different for each compound.

On the whole, the most reasonable conclusions are that there is no out-of-plane deflection in them, and that conventional van der Waals radii, or at least that for the methyl group, are too large in this context. It is obvious that the relevant value is a function of the problem into which it enters, because atoms must be regarded as compressible and not as rigid spheres. So, when we are considering the stopping of free rotation, we need a radius which corresponds to a compressional energy of about 600 cals./mols; but when we are considering the bending of a bond through 12°, we need one which corresponds to a compressional energy of about 1—2 kcals./mole. The former radius will obviously be larger than the latter, though until we know the typical energy–radius relation we cannot say what the difference is. It is possible that results such as are now communicated may lead to a more quantitative understanding of the forces between non-bonded atoms.

## EXPERIMENTAL.

*Preparation and Purification of Materials.—Benzene.* " AnalaR " benzene was purified by freezing out thrice, drying ($P_2O_5$), and distilling it over the same drying agent in a stream of dry air, under which it was stored until required.

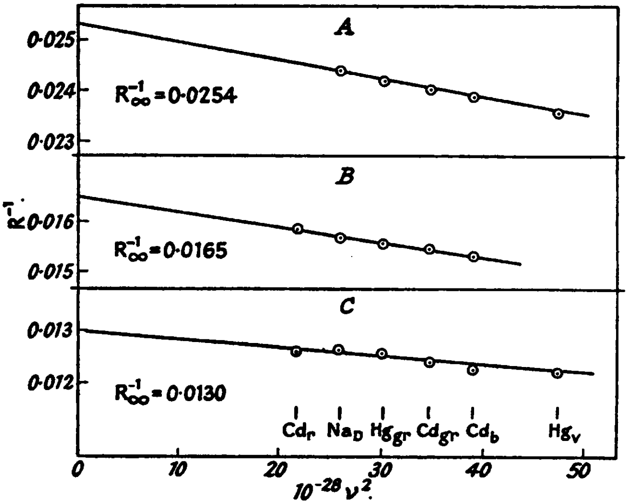
p-*Dibromobenzene.* A commercial specimen was recrystallized several times, and finally sublimed in a vacuum. It had m. p. 89° (Jaeger, *Z. anorg. Chem.*, 1917, **101**, 122, give 89°).

p-*Di*-tert.-*butylbenzene.* This was prepared by the method of Ipatief, Corson, and Pines (*J. Amer. Chem. Soc.*, 1936, **58**, 919). It was recrystallized from methanol and purified chromatographically. It had m. p. 77·5—78·0° as required (*loc. cit.*).

2 : 5-*Dibromo*-1 : 4-*di*-tert.-*butylbenzene.* This substance was obtained in a small yield (5%) by bromination of the hydrocarbon in glacial acetic acid with iodine as a catalyst. Several other products were formed and the purification was difficult. It was more conveniently prepared by a method of bromination suggested by Derbyshire and Waters (*Nature*, 1949, **164**, 446; *J.*, 1950, 573) : *p*-di-*tert.*-butylbenzene (0·053 mole) was dissolved in glacial acetic acid (300 c.c.) containing bromine (0·1 mole). The solution was made 2N. with respect to nitric acid and stirred mechanically in a double-necked flask. A solution of silver nitrate (17 g. in 50 c.c. of water) was added (1 hour), and a vigorous action took place. The reaction mixture was diluted with water, freed from residual bromine, neutralized, and extracted with ether. The dried ethereal extract was fractionally distilled at 14 mm. The highest-boiling fraction (232°) solidified on cooling and recrystallized from ether and ethanol as colourless plates, m. p. 107°. The *dibromo*-compound was subjected to chromatographic analysis and found to be pure and homogeneous [Found (analysis by Drs. Weiler and Strauss, Oxford) : C, 48·4; H, 5·8; Br, 45·8. $C_{14}H_{20}Br_2$ requires C, 48·3; H, 5·8; Br, 45·9%].

FIG. 5.

*Dispersion of refractive index.*



A. p-*Dibromobenzene.* B. p-*Di*-tert.-*butylbenzene.* C. 2 : 5-*Dibromo*-1 : 4-*di*-tert.-*butylbenzene.*

*Physical Measurements.*—These were carried out essentially as described in previous publications (*e.g.*, *J.*, 1949, 2312) and the symbols have the same significance. The refractive index of a solution relative to that of benzene was measured with a Pulfrich refractometer, fitted with a divided cell. The molar refraction $[R]_D$ for the sodium line was determined for 2—5 different solutions. Dispersion measurements with the principal lines in the cadmium and the mercury spectrum were carried out in the most concentrated solution; $[R]_\lambda$ was computed and plotted reciprocally against the squared frequency, $\nu^2$ (Fig. 5). The refraction $[R]_\infty$ for infinite wave-length was obtained by graphical extrapolation to $\nu^2 = 0$. For the computation of $[R]_2$ it is necessary to know the absolute value of the specific polarisation $p_1$ of benzene. No consistent set of values for the series of wave-lengths used could be found in the literature; $p_1$ was therefore obtained in the following way. A series of absolute refractometer readings for the benzene side of the divided cell was taken from one of the sets of results (2 : 5-dibromo-1 : 4-di-*tert.*-butylbenzene). Extra care was taken to ensure temperature constancy during these measurements. The refractive indices $n_1$ for the set of wave-lengths thus obtained were reliable relatively to each other, whereas the absolute value was somewhat affected by the shape of the layer of contact liquid between the prisms and the cell. The readings were therefore all normalized to the well-established standard value 1·49800 for the sodium *D* line. From this set of $n_1$ values and the standard value 1·14515 of the specific volume of benzene at 25°, $p_1$ was computed; whereafter $[R]_2$ was calculated by means of the mixture law and the molecular weight $M_2$.

## RESULTS.

2 : 5-*Dibromo*-1 : 4-*di*-tert.-*butylbenzene.*

| $10^5\omega$. | ε. | *v*. | $10^5\Delta n_D^{25}$. | $[R]_D$, cm.$^3$. | $10^5\omega$. | ε. | *v*. | $10^5\Delta n_D^{25}$. | $[R]_D$, cm.$^3$ |
|---|---|---|---|---|---|---|---|---|---|
| 0 | (2·2727) | 1·14515 | — | — | 1031 | 2·2745 | 1·14063 | 38 | 79·3 |
| 244 | 2·2731 | 1·14410 | — | — | 1263 | 2·2746 | 1·13967 | 42 | 78·2 |
| 611 | 2·2739 | 1·14239 | 26 | 80·3 | 1652 | 2·2751 | 1·13776 | 63 | 79·4 |
| 814 | 2·2742 | 1·14158 | 29 | 79·1 | | from dispersion measurements | | | 79·1 |

$\varepsilon = 2{\cdot}2729 + 0{\cdot}143\omega$; $v = 1{\cdot}14518 - 0{\cdot}445\omega$; ${}_TP = 81{\cdot}9 \pm 0{\cdot}5$ cm.$^3$; $[R]_D$ (average) $= 79{\cdot}2 \pm 0{\cdot}1$ cm.$^3$.

p-*Dibromobenzene.*

| $10^5\omega$. | ε. | *v*. | $10^5\Delta n_D^{25}$. | $[R]_D$, cm.$^3$. | $10^5\omega$. | ε. | *v*. | $10^5\Delta n_D^{25}$. | $[R]_D$, cm.$^3$ |
|---|---|---|---|---|---|---|---|---|---|
| 345 | 2·2730 | 1·14293 | — | — | 1459 | 2·2748 | 1·13542 | 75 | 41·0 |
| 679 | 2·2740 | 1·14065 | 34 | 40·8 | 1554 | 2·2753 | 1·13509 | 79 | 41·0 |
| 1037 | 2·2742 | 1·13848 | 53 | 41·0 | | from dispersion measurements | | | 41·0 |

$\varepsilon = 2{\cdot}2727 + 0{\cdot}157\omega$; $v = 1{\cdot}14510 - 0{\cdot}650\omega$; ${}_TP = 41{\cdot}8 \pm 0{\cdot}5$ cm.$^3$; $[R]_D$ (average) $= 41{\cdot}0 \pm 0{\cdot}1$ cm.$^3$.

p-*Di*-tert.-*butylbenzene.*

| $10^5\omega$. | ε. | *v*. | $10^5\Delta n_D^{25}$. | $[R]_D$, cm.$^3$. | $10^5\omega$. | ε. | *v*. | $10^5\Delta n_D^{25}$. | $[R]_D$, cm.$^3$ |
|---|---|---|---|---|---|---|---|---|---|
| 464 | 2·2723 | 1·14528 | — | — | 1990 | 2·2723 | 1·14549 | −28 | 63·73 |
| 822 | 2·2727 | 1·14531 | — | — | 3174 | 2·2717 | 1·14594 | −47 | 63·67 |
| 1248 | 2·2723 | 1·14540 | — | — | | | | | |

$\varepsilon = 2{\cdot}2727 - 0{\cdot}028\omega$; $v = 1{\cdot}14508 + 0{\cdot}026\omega$; ${}_TP = 65{\cdot}3 \pm 0{\cdot}4$ cm.$^3$; $[R]_D$ (average) $= 63{\cdot}7 \pm 0{\cdot}1$ cm.$^3$.

*Dispersion results* (25°).

| | $Cd_r$. | $Na_D$. | $Hg_g$. | $Cd_g$. | $Cd_b$. | $Hg_v$. |
|---|---|---|---|---|---|---|
| λ (A.) | 6438 | 5893 | 5461 | 5086 | 4800 | 4358 |
| $10^{-28}\ \nu^2$ | 21·67 | 25·86 | 30·12 | 34·72 | 38·98 | 47·28 |
| $n_1$ | 1·49398 | 1·49800 | 1·50197 | 1·50648 | 1·51077 | 1·51959 |
| $p_1$ | 0·33337 | 0·33567 | 0·33793 | 0·34050 | 0·34293 | 0·34790 |

2 : 5-*Dibromo*-1 : 4-*di*-tert.-*butylbenzene* ($\omega = 0{\cdot}01652$).

| | $Cd_r$. | $Na_D$. | $Hg_g$. | $Cd_g$. | $Cd_b$. | $Hg_v$. |
|---|---|---|---|---|---|---|
| $10^5 . \Delta n$ | 71 | 65 | 63 | 69 | 74 | 65 |
| $[R]_2$ | 79·4 | 79·1 | 74·5 | 80·6 | 81·7 | 81·8 |
| $[R]_2^{-1}$ | 0·01259 | 0·01264 | 0·01258 | 0·01241 | 0·01224 | 0·01222 |

p-*Dibromobenzene* ($\omega = 0{\cdot}01459$).

| | $Cd_r$. | $Na_D$. | $Hg_g$. | $Cd_g$. | $Cd_b$. | $Hg_v$. |
|---|---|---|---|---|---|---|
| $10^5 . \Delta n$ | 70 | 75 | 75 | 77 | 77 | 77 |
| $[R]_2$ | 40·3 | 41·0 | 41·3 | 41·7 | 41·9 | 42·5 |
| $[R]_2^{-1}$ | 0·02480 | 0·02438 | 0·02420 | 0·02401 | 0·02386 | 0·02353 |

p-*Di*-tert.-*butylbenzene* ($\omega = 0{\cdot}01990$).

| | $Cd_r$. | $Na_D$. | $Hg_g$. | $Cd_g$. | $Cd_b$. | $Hg_v$. |
|---|---|---|---|---|---|---|
| $10^5 . \Delta n$ | −28 | −28 | −28 | −28 | −28 | |
| $[R]_2$ | 63·3 | 63·7 | 64·2 | 64·7 | 65·2 | |
| $[R]_2^{-1}$ | 0·01581 | 0·01569 | 0·01557 | 0·01546 | 0·01534 | |

The authors are indebted to Dr. J. A. Barltrop and Mr. L. E. Orgel for advice and discussion; and to Imperial Chemical Industries Limited for a grant towards the cost of research. One of them (H. K.) records his thanks to The British Council for a Scholarship.

PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, March* 12*th*, 1951.]