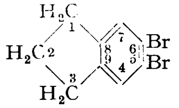
324. *A Contribution to the Study of the Mills–Nixon Effect. Dipole Moments of* 1 : 3-*Dioxaindane,* 1 : 4-*Dioxatetralin, and of Some of Their Nitro- and Bromo-derivatives.*

By H. D. Springall and G. C. Hampson, and (in part) C. G. May and H. Spedding.

A short summary of the work on the Mills–Nixon effect is given. The dipole moments of 1 : 3-dioxaindane and 1 : 4-dioxatetralin are interpreted in terms of the facility of electron release from the side rings to the aromatic nuclei. The observed differences are correlated with relative stereochemical stabilities of the excited ionic structures contributing to the molecules. The investigation is extended to the 5-nitro- and 5 : 6-dibromo-dioxaindanes and 6-nitro- and 6 : 7-dibromo-dioxatetralins. An analysis of the interaction moments is given which confirms the findings on the unsubstituted compounds.

Mills and Nixon (*J.*, 1930, 2510) postulated, on stereochemical grounds, the fixation of the double bonds in the benzene nuclei of indane (hydrindene) (dicyclic, 8 : 9-bond single) and tetralin (dicyclic, 9 : 10-bond double), the stereochemical argument being much stronger in the case of indane. They adduced evidence for this fixation from observations of the chemical reactivity in coupling and bromination reactions of 5-substituted indanes and 6-substituted tetralins. This line of investigation was subsequently developed by Fieser and Lothrop (*J. Amer. Chem. Soc.*, 1936, **58**, 2050; 1937, **59**, 945) and by McLeish and Campbell (*J.*, 1937, 1103).

The work recorded below, on 1 : 3-dioxaindane and 1 : 4-dioxatetralin derivatives, begun in Oxford in 1933, was designed to amplify the investigation, started at the same time, of the Mills–Nixon effect by consideration of the dipole moments of 5 : 6-dibromoindane (I) and 6 : 7-dibromotetralin (II). As these two compounds proved somewhat inaccessible, the corresponding 5 : 6-dibromo-1 : 3-dioxaindane (III) and 6 : 7-dibromo-1 : 4-dioxatetralin (IV) were investigated. These compounds are formally analogous to the dibromo-indane and -tetralin and should show similar stereochemical side-ring effects; they have, moreover, the advantage of being much more readily accessible. The resultant dipole moments for these dioxa-compounds are, however, complicated by overlapping and opposed electromeric effects, and the interpretation of the results was deferred until the electrometrically less complex systems of the indane and tetralin series had been further investigated.



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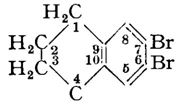

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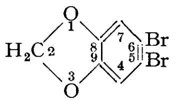

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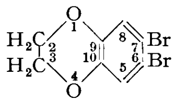


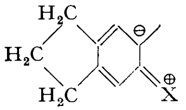
(IV.)

The preparation and dipole-moment investigation on the bromo-indane and -tetralin was completed in 1936 (Sidgwick and Springall, *J.*, 1936, 1532) and the dipole results interpreted provisionally as indicating probable bond fixation in indane (dicyclic, 8 : 9-bond single; component of moment due to Br·C·C·Br system = 1·78 D.; angle between bonds C_5–Br and C_6–Br, $\theta = 75° \pm 5°$), but free Kekulé resonance in tetralin (dicyclic, 9 : 10-bond aromatic; component of moment due to Br·C·C·Br system = 2·11 D.; angle between bonds C_6–Br and C_7–Br, $\phi = 60°$).

The work of Dolliver, Gresham, Kistiakowsky, and Vaughan (*J. Amer. Chem. Soc.*, 1937, **59**, 831) on the heats of hydrogenation of indane and various alkyl derivatives of benzene showed that the benzene ring in indane is in fact stabilised by resonance by 42-kcals./mole, indicative of full Kekulé resonance and quite precluding bond fixation.

Sutton and Pauling (*Trans. Faraday Soc.*, 1935, **31**, 939) had given a quantum-mechanical treatment to the Mills–Nixon effect problem, using the method of atomic orbitals. They showed that the chemical reactivity observations, which had been used as original evidence for bond fixation, could be explained in terms of activation energy changes, due to stereochemical strain effects stabilising, to a small extent, certain of the ionic excited structures, without invoking rigid fixation of aromatic nuclei in one or other of the Kekulé forms. Thus, the slight stabilisation, by the 5- and 6-membered rings respectively, of the excited structures (V) and (VI) is sufficient to account for the results of the coupling and bromination experiments.

These two lines of work rendered more urgent the application, which it had always been our intention to make, of a check on the interpretation of the dipole results as implying bond fixation in indane. This check was the measuring of the Br ⟷ Br distance in the dibromoindane and related compounds by means of electron diffraction. The Br ⟷ Br distance in the indane derivative should be greater (calculated value 3·70 A.) if the 8 : 9-bond were indeed a fixed single bond ($\theta = 75°$) than the corresponding Br ⟷ Br distance (calculated value 3·39 A.) in *o*-dibromobenzene. When the electron-diffraction investigation was carried through (Kossiakoff and Springall, *J. Amer. Chem. Soc.*, 1941, **63**, 2223; Springall, *Chem. and Ind.*, 1943, **21**, 149) it was found that the Br ⟷ Br distances in the dibromo-indane, -tetralin, -*o*-xylene, and -benzene were identical (found value 3·39±0·02 A.), thus confirming the free resonance in indane, to be expected from the work of Kistiakowsky and of Sutton and Pauling, and necessitating a reconsideration of the dipole-moment findings for the dibromo-indane and -tetralin in terms of $\theta = \phi = 60°$.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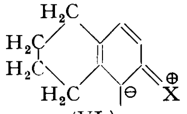
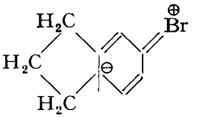
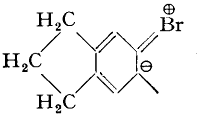
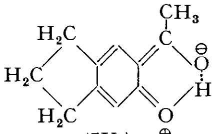

(VI.)

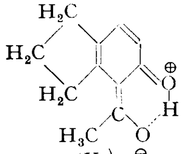
(X = NHAc or OH.)

An interpretation of the low value of the Br·C·C·Br moment in the indane derivative in terms of changes in the stabilisation of ionic excited structures, following lines similar to those of Sutton and Pauling (*loc. cit.*), was offered by Kossiakoff and Springall, who suggested that the slight stabilisation by the Mills–Nixon strain of the side ring of structures such as (VII) and (VIII) could be responsible for the lowering of the Br·C·C·Br moment in 5 : 6-dibromoindane.


(VII.)


(VIII.)

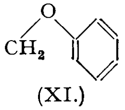

(IX.) ⊕


(X.) ⊖

Baker's observation (*J.*, 1937, 477) of strong chelation in 5-hydroxy-6-acetylindane, and weak chelation in 5-hydroxy-4-acetylindane may be given a similar explanation in terms of the effect of the side ring on the stability of the ionic excited *o*-quinonoid structures (IX) and (X), the former being somewhat stabilised, and the latter somewhat destabilised.

In recent years the Mills–Nixon problem has been the subject of two theoretical investigations by the method of molecular orbitals. Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 906) reconciled the reactivity of 5-substituted indanes with the virtual retention of Kekulé resonance in the aromatic ring, by consideration of the resonance integral of the dicyclic 8 : 9-bond. He envisages the possibility that the effect of the side ring is to stretch this bond. Longuet-Higgins and Coulson (*Trans. Faraday Soc.*, 1946, **42**, 756) conclude that the steric effects of the side ring on the aromatic ring are to compress the bonds 7 : 8, 8 : 9, and 9 : 4 and to stretch the bonds 4 : 5, 5 : 6, and 6 : 7 of the aromatic ring. They develop from this point an alternative explanation of the activation energy effects responsible for the chemical reactivity observations, in terms of transition-complex stabilisation. This explanation has a formal resemblance to Kossiakoff and Springall's suggestion (*loc. cit.*) concerning the reconciliation of the dimensions and dipole moments of the dibromo-compounds, but Longuet-Higgins and Coulson are sceptical of the latter suggestion, though they do not advance an alternative.

Independently of work on the Mills–Nixon effect, the study of dipole moment results with the system (XI) has been considerably developed since 1933.



(XI.)

The work of Bergmann, Engel, and Sandor (*Z. physikal. Chem.*, 1930, *B*, **10**, 397), Bergmann and Tschudnowsky (*ibid.*, 1932, *B*, **17**, 107), Hampson and Sutton (*Proc. Roy. Soc.*, 1933, *A*, **140**, 562), Hampson, Sutton, and Farmer (*ibid.*, 1933, *A*, **143**, 147), Bennett (*Trans. Faraday Soc.*, 1934, **30**, 853), and Marsden and Sutton (*J.*, 1936, 599) on the dipole moments in the anisole series has led to the evaluation of (*a*) the interaction moments for various 4-substituted anisoles, (*b*) the angle θ_2 which the dipole moment of anisole (1·23 D.) makes with O–phenyl bond ($\theta_2 = 76°$).

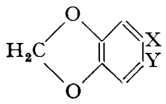
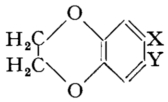
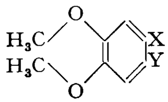
All this work provides a background against which it is possible to offer some explanation of the dipole-moment results obtained with the dioxa-indane and -tetralin derivatives.

The compounds examined were 1 : 3-dioxaindane and its 5-nitro- and 5 : 6-dibromo-derivatives, and 1 : 4-dioxatetralin and its 6-nitro- and 6 : 7-dibromo-derivatives.

The dipole-moment results for these compounds are given in Table I.

TABLE I.

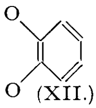
(Moments in D.)

	X = Y = H.	X = H, Y = NO_2.			X = Y = Br.		
Type.	μ.	μ (molecular).	NO_2 component.*	$\Delta\mu_{NO_2}$.*	μ (molecular).	Br·C·C·Br component.†	$\Delta\mu_{(Br)_2}$.†
	0·80	4·80	4·33	0·36	2·61	1·81	−0·31
	1·42	5·40	4·55	0·58	4·00	2·58	0·46
 Calculated model.	1·37	5·18	4·34	0·37	3·75	2·38	0·26

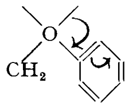
* Acting along the C–N bond.
† Acting along the axis of symmetry of the molecule.

The discussion of these results falls into two sections : the dipole moments of (1) the dioxa-side-rings, (2) the $C{\cdot}NO_2$ and Br·C·C·Br systems.

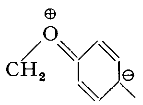
(1) *The Dioxa-side-ring Moments.*—(*a*) *Direction.* The molecular fragment (XII) must be planar, in both dioxaindane and dioxatetralin. The effect (XIII) will tend (i) to keep the CH_2 in the plane of the $O-C_6H_5$ and (ii) to increase the $C-\hat{O}-C$ angle above 110°. The operation of these two factors will cause the whole molecule of dioxaindane and probably that of dioxatetralin to be planar. (The molecular structure of these compounds will be determined by electron diffraction, to settle this point.) Even if the factors are not strong enough to hold the dioxatetralin rigidly planar, they will prevent any marked departures from that configuration. Symmetry considerations then necessitate that the resultant side-ring moments must act in the plane of the benzene nucleus and perpendicular to the dicyclic bond. From analogy with the anisole series it is almost certain that the sense of the side-ring moments must be with the negative ends towards the benzene ring. This is settled by the results for the mononitro- and dibromo-derivatives of the dioxa-compounds, which are compatible only with this assignment



(XII.)



(XIII.)



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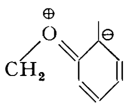

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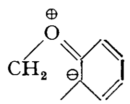


(XVI.)

of sense to the side-ring moments. This sense of the side-ring moments indicates that, as would be expected on general grounds, the ionic excited structures (XIV), (XV), and (XVI) contribute to the overall molecular structure.

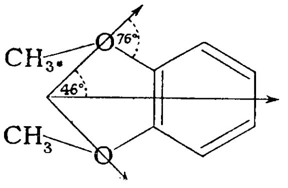
(*b*) *Magnitude.* It seems desirable to treat the dioxa-side-ring moments in terms of the moments for anisole and veratrole. The marked difference in magnitude between the moments of the 5- and the 6-membered side rings must come under consideration.

The specific planar configuration (XVII) of veratrole is taken as a model for the dioxa-ring compounds. The dipole-moment vector data for anisole enable the resultant moment of the configuration of veratrole (XVII) to be evaluated approximately by the expression

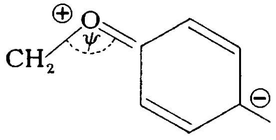
$$\mu_{\text{XVII}} = [2(1{\cdot}23 \cos 46^\circ)] \times 0{\cdot}8 = 1{\cdot}37 \text{ D.}$$

(the factor 0·8 allows roughly for the "ortho-effect"—the mutual polarisation effect which depresses the resultant moment of two *o*-groups below the vector sum value; see, *e.g.*, Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919; Sidgwick and Springall, *loc. cit.*).

The observed moment for 1 : 4-dioxatetralin, 1·42 D., is somewhat larger than the calculated "model" value. No great significance can be attached directly to the difference between 1·42 and 1·37 D. (especially in view of the approximations involved in the derivation of the calculated 1·37 D. value). Yet the difference may be real, for there is other evidence, from the nitrated and brominated compounds (see below), indicating that the electromeric or mesomeric release of electrons to the benzene nucleus from the oxygen atoms [by the participation of structures (XIV), (XV), and (XVI)] is more facile with the 6-membered dioxa-side-ring than with the methoxy-groups.



(XVII.)



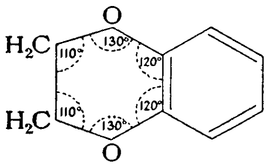
(XVIII.)

The observed moment for 1 : 3-dioxaindane, 0·80 D., is much lower than the calculated "model" value, indicating that electron release to the benzene nucleus is much less facile with the 5-membered dioxa-side ring than with the methoxy-groups.

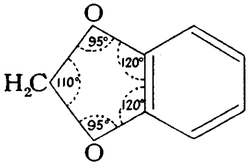
It is possible to suggest a treatment of these variations based on the following factors :

(i) The restriction, by ring closure, of free rotation about the $O-C_6H_5$ bonds in both the dioxa-side rings would help to stabilise the ionic excited structures (XIV), (XV), (XVI), etc., in these compounds relative to corresponding structures for the methoxy-compounds.

(ii) The ionic structures (XIV), (XV), and (XVI) involve the formation of a double bond in the side ring. The stereochemistry of the 6-membered ring favours this, while that of the 5-membered ring opposes it. Thus, in the ionic system (XVIII) the unstrained value for the angle ψ will be in the range 120—130°. This will be readily achieved in the 6-membered dioxa-side ring, but cannot be achieved in the 5-membered side ring. The angular dimensions shown

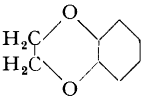


(XIX.)

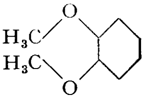


(XX.)

in (XIX) and (XX) have been derived then by assigning all angular strain to the $\widehat{\mathrm{COC}}$ angle. (The work of Hampson and Sutton, *loc. cit.*, and Hampson, Sutton, and Farmer, *loc. cit.*, indicates that much less energy is required to change the $\mathrm{O}{<}$ angle than the $\mathrm{CH_2}{<}$ angle.) It is probable that the strain is to some extent shared by the $\mathrm{C}{<}$ angle, but (XIX) and (XX) show qualitatively how the 6-membered side ring favours, and the 5-membered ring opposes, the large $\widehat{COC}$ angle needed for the participation of structures (XIV), (XV), and (XVI).



(XXI.)



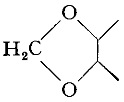
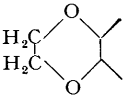
(XXII.)

(iii) In the 5-membered dioxa-side ring both the $CH_2{\longrightarrow}O$ bond moments have their positive poles on the same C atom. Mutual polarisation would tend to reduce these $CH_2{<}\genfrac{}{}{0pt}{}{O}{O}$ bond moments relative to those of the systems (XXI) and (XXII). The effects of these factors are summarised in Table II.

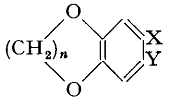
It seems not unreasonable to regard the observed high moment of the 6-membered ring as largely accounted for by factors (i) and (ii), and the low moment of the 5-membered ring as due to factors (ii) and (iii) preponderating over (i).

TABLE II.

Effect of factor on moment of side ring.

Side-ring type.	Factor (i).	Factor (ii).	Factor (iii).
	Increases	Decreases	Decreases
	Increases	Increases	—

(2) *The Moments of the* $C{\cdot}NO_2$ *and* $Br{\cdot}C{\cdot}C{\cdot}Br$ *Systems.*—The mononitro-compounds of the dioxa-indane and -tetralin were investigated primarily to settle unequivocally the sense of the dioxa-side-ring moments; but the results are of some interest in themselves in that they give some light on the nature of the electromeric (mesomeric) conjugation interactions between the side ring and the groups X and Y in the general system (XXIII). In connection with these interactions the following are the starting points :

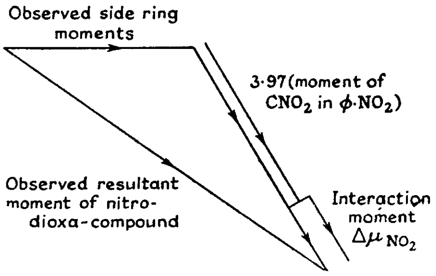


(XXIII.)

(*a*) From Kossiakoff and Springall's results (*loc. cit.*) on the dimensions of the indane and tetralin derivatives it is highly probable that in the dioxa-compounds (XXIII) the C–X and C–Y bonds make the normal aromatic angle of 120° with the adjacent aromatic bonds.

(*b*) Conjugated electromeric (mesomeric) interactions may occur between Y and the atom O *para* to Y, but not between Y and the O atom *meta* to Y.

From these considerations it is possible to construct the following simple vector model for the component moments of the nitro-compounds and to evaluate from this the mesomeric interaction moments, $\Delta\mu_{NO_2}$ operating along the C–N bond, between the dioxa-side ring and the C–NO$_2$ group.



The resultant moments and the derived interaction moments for the (side-ring–NO$_2$) systems are given in Table I and are compared there with the corresponding data calculated for the

4-nitro-derivative of the specific configuration (XVII) of veratrole, using the known interaction moment 0·37 D. for *p*-nitroanisole (Marsden and Sutton, *loc. cit.*).

The values found for $\Delta\mu_{NO_2}$ indicate that ease of release of electrons to the aromatic system by the contribution of structure (XIV) is in the order 6-membered dioxa-ring > veratrole model > 5-membered dioxa-ring. This is the same order as was deduced from the moments of the unsubstituted compounds, though no individual significance can be attached to the difference between $\Delta\mu_{NO_2}$ for the veratrole model, 0·37 D., and for the 5-membered ring compound, 0·36 D.

These considerations enable some treatment to be given to the problem of the dipole moments of the Br·C·C·Br systems of 5 : 6-dibromo-1 : 3-dioxaindane and 6 : 7-dibromo-1 : 4-dioxatetralin (*i.e.*, the components of the resultant molecular moments due to the Br·C·C·Br systems).

In each of the compounds, the side-ring moment, the normal aromatic *o*-dibromo-moment, and any side-ring–Br interaction moment must, from symmetry considerations, all act along the same axis, that of the symmetry of the molecules, so that the required components are given by

$$\mu_{\mathrm{Br\cdot C\cdot C\cdot Br}} = \mu_{\mathrm{molec.}} - \mu_{\mathrm{side\ ring}}$$

The values of these $\mu_{\mathrm{Br\cdot C\cdot C\cdot Br}}$ are listed in Table I.

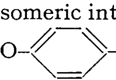
Each of these $\mu_{\mathrm{Br\cdot C\cdot C\cdot Br}}$ terms may be regarded as made up of the normal aromatic *o*-dibromo-moment, the moment of *o*-dibromobenzene, 2·12 D. (Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 135), and the mesomeric interaction moment between the Br·C·C·Br system and the dioxa-side-ring, $\Delta\mu_{(Br)_2}$.

These interaction moments are given by

$$\Delta\mu_{(Br)_2} = \mu_{\mathrm{Br\cdot C\cdot C\cdot Br}} - 2{\cdot}12$$

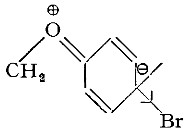
The values of the interaction moments are given in Table I.

From this point of view the problem is resolved into that of treating the variations in $\Delta\mu_{(Br)_2}$.

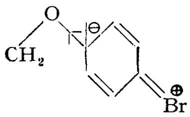
The values of $\Delta_{(Br)_2}$ derived from the observed moments of the dibromo-dioxa-compounds are compared in Table I with the reference value calculated for the corresponding 4 : 5-dibromo-derivative of the veratrole molecule (XVII), the calculation being made as follows. The work of Bennett (*loc. cit.*) and Marsden and Sutton (*loc. cit.*) has shown that the mesomeric interaction moment operating in *p*-bromoanisole has magnitude 0·15 D. acting along the O––Br axis, the negative end being towards the Br atom. This, taken with the general points made above in considering the $\Delta\mu_{NO_2}$ values, permits the calculation of the interaction moment $\Delta\mu_{(Br)_2}$ for 4 : 5-dibromoveratrole in the specific (XVII) configuration. In this case $\Delta\mu_{(Br)_2} = 2 \times 0{\cdot}15 \cos 30° = 0{\cdot}26$ D.

The " observed " value of $\Delta\mu_{(Br)_2}$ for the 6-membered side-ring compound, 0·46 D., is considerably higher than the model value, whereas for the 5-membered side-ring compound the value of $\Delta\mu_{(Br)_2}$, −0·31 D., is actually in the reverse sense to that of the model value.

In all these bromo-compounds the interaction moment is determined by a complex system of overlapping and opposed electromeric (mesomeric) effects, which can only be analysed qualitatively at present.



(XXIV.)



(XXV.)

(*a*) The strong inductive effect of the C—>—Br bond tends to increase the contribution of the ionic structures (XIV), etc., above the value for the unbrominated compound by promotion of structures of the type (XXIV), giving an interaction effect $\overset{+\!\longrightarrow}{\mathrm{O}\!-\!\!-\!\!-\mathrm{Br}}$.

(*b*) The normal electromeric effect in the $\mathrm{C_6H_5}\overset{\curvearrowleft}{-\!\!-}\mathrm{Br}^{-}$ system assisted by the inductive effect in the O—<—C bond tends to decrease contributions of the ionic structures (XIV), etc., below the value for the unbrominated compound by promotion of structures of the type (XXV), giving an interaction effect of the type $\overset{\longleftarrow\!+}{\mathrm{O}\!-\!\!-\!\!-\mathrm{Br}}$

The work on *p*-bromoanisole and the rough calculations on the dibromoveratrole model show that, as would be expected, in the absence of steric complications due to side-ring formation, the $\overset{+\longrightarrow}{\text{O——Br}}$ interaction predominates over the $\overset{\longleftarrow+}{\text{O——Br}}$ interaction. The present results show that this $\overset{+\longrightarrow}{\text{O——Br}}$ predominance is increased by the closure of the 6-membered ring, but that the resultant interaction effect is reversed ($\overset{\longleftarrow+}{\text{O——Br}}$ predominating over $\overset{+\longrightarrow}{\text{O——Br}}$) by the closure of the 5-membered ring.

The following possible explanation of these effects is offered. (*a*) The above consideration of the dipole results for the unsubstituted compounds and the mononitro-derivatives indicates that the ease of electron release from the oxygen atom to the benzene ring is in the order 6-membered dioxa-ring > veratrole model > 5-membered dioxa-ring [contribution of structures (XXIV) decreasing], so that from this point of view the $\overset{+\longrightarrow}{\text{O——Br}}$ interaction effect should *decrease* in passing from dibromodioxatetralin through the dibromoveratrole model to the dibromodioxaindane. (*b*) The interpretation offered by Kossiakoff and Springall for the low moment of the Br·C·C·Br system in dibromoindane would lead to the view that the ease of electron release from the bromine atom to the benzene ring is in the order dibromodioxatetralin < dibromoveratrole < dibromodioxaindane [contribution of structures (XXV) increasing], so that the $\overset{\longleftarrow+}{\text{O——Br}}$ interaction effect should *increase* in passing from the dibromodioxatetralin through the dibromoveratrole model to the dibromodioxaindane.

These two trends (*a*) and (*b*) would account for the observed variations in $\Delta\mu_{(\mathrm{Br})_2}$ interaction moment values in terms of reasonable variations in the contributions of ionic recited structures, due to steric effects of the Mills–Nixon type, but without any appeal to rigid bond fixation.

EXPERIMENTAL.

Preparation of Materials.—*Benzene.* Hopkin and Williams's thiophen-free benzene was frozen out four times, heated under reflux over phosphoric oxide, and distilled in a current of dry air into a receiver from which it could be pumped for immediate use.

1 : 3-*Dioxaindane.* Methylene sulphate was prepared by the action of fuming sulphuric acid on paraformaldehyde by the method of Delépine (*Compt. rend.*, 1899, **129**, 831; *Bull. Soc. chim.*, 1899, **21**, 1055) and Delaby (*ibid.*, 1926, **39**, 1612) as modified by Baker (*J.*, 1931, 1765). 1 : 3-Dioxaindane was prepared by the action of methylene sulphate on a mixture of catechol in acetone and sodium hydroxide in water (*idem, ibid.*, p. 1767). It distilled as a colourless oil, the fraction of b. p. 173°/756 mm. being used (Baker gives b. p. 173—174°/756 mm.).

1 : 4-*Dioxatetralin.* This was prepared by the action of ethylene dibromide on catechol, either (*a*) by using potassium hydroxide and water (Vorländer, *Annalen*, 1894, **280**, 205; Gattermann, *ibid.*, 1907, **357**, 373), or (*b*) by using potassium carbonate, copper bronze, and glycerol (Ghosh, *J.*, 1915, **107**, 1591). The compound distilled as a colourless oil at 212—216°/750 mm. The fraction of b. p. 99—100°/7 mm. was used (Gattermann gives b. p. 99—100°/7 mm.).

5-*Nitro*-1 : 3-*dioxaindane.* Piperonal was nitrated directly by nitric acid (*d* 1·42), and the required compound was separated from admixed nitropiperonal by the bisulphite reaction (Salway, *J.*, 1909, **95**, 1163). The product, recrystallised from alcohol, had m. p. 145° (Salway gives 145°; Jobst and Hesse, *Annalen*, 1879, **199**, 74, give 148°).

6-*Nitro*-1 : 4-*dioxatetralin.* 1 : 4-Dioxatetralin was nitrated by nitric acid (*d* 1·5), both in glacial acetic acid solution (Vorländer, *loc. cit.*). The product was recrystallized from alcohol; m. p. 122° (Vorländer gives m. p. 121°).

5 : 6-*Dibromo*-1 : 3-*dioxaindane.* Piperonylic acid was prepared by oxidation of piperonal by aqueous potassium permanganate (Fittig and Mielch, *Annalen*, 1869, **152**, 40), and its solution in aqueous sodium carbonate was brominated by means of bromine water (Robinson, *J.*, 1917, **111**, 913). The precipitated dibromo-compound was recrystallised from alcohol; colourless leaflets, m. p. 86° (Robinson, *loc. cit.*, gives m. p. 86°).

6 : 7-*Dibromo*-1 : 4-*dioxatetralin.* This was prepared by drawing the calculated quantity of bromine vapour, mixed with air, through a solution of 1 : 4-dioxatetralin in glacial acetic acid, at room temperature. The compound crystallised from the reaction mixture; it was collected, washed with water, and recrystallised from alcohol; m. p. 138° (Ghosh, *loc. cit.*, gives m. p. 138°).

Dipole-moment Determinations.—These determinations were made in benzene solution at 25° by the refractivity method, the heterodyne technique being used for the measurement of dielectric constant. Most of the measurements were carried out in Oxford (1934—1936), using the apparatus described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668), Hampson, Farmer, and Sutton (*ibid.*, 1933, *A*, **143**, 147), Jenkins (*J.*, 1934, 481), and Jenkins and Sutton (*J.*, 1935, 609).

Some of the measurements on dioxa-indane and -tetralin were carried out in Manchester (1948), using a much more highly developed circuit for the measurement of dielectric constant. This circuit has been entirely based on a design prepared by Dr. L. E. Sutton and Dr. R. A. W. Hill in Oxford, and as the whole arrangement of the Oxford prototype will be discussed by them in a forthcoming publication, we only mention here the salient features. The measuring cell (as described by Jenkins and Sutton, *loc. cit.*) forms part of the variable oscillator circuit of a beat frequency oscillator (" B.F.O.") of which the fixed oscillator operates at a frequency of 500 kc. The B.F.O. output is taken to the X-plates of a cathode-ray oscillograph (" C.R.O."), the Y-plates of which are fed from a fixed 1 kc. oscillator. The variable oscillator of the B.F.O. is tuned to 500 — 1 kc., the tuning being followed on the C.R.O. The measuring cell is then replaced, by means of a special low-capacity switch, in the variable oscillator of the B.F.O. by a standard Muirhead variable air condenser (Type A-411-F, 250 $\mu\mu$F.). The variable oscillator is then re-tuned to 500 — 1 kc., using the standard condenser alone. The capacity of the tuned standard condenser is then identical with that of the measuring cell. The equivalence of the two capacities is checked by the interchange of the measuring cell and the tuned standard condenser, no effect being produced on the C.R.O. figure. Special care is taken in the design of the H.T. power-packs, to ensure that the H.T. supply to the B.F.O. oscillators and the 1 kc. oscillator is completely stable to mains variations.

The results are given in the accompanying tables.

1 : 3-*Dioxaindane.*

f_2.	d_s.	ε.	n^2.	P_2.	${}_{\mathrm{E}}P_2$.
0·045212	0·8896	2·32040	2·26473	46·32	33·13
0·040521	0·8882	2·31570	2·26392	45·60	32·92
0·029828	0·8842	2·30415	2·26214	46·34	32·95
0·027885 *	0·88453	2·3060	2·2593	47·27	33·30
0·024002	0·8823	2·29848	2·26109	46·38	32·89
0·015731	0·8793	2·28900	2·25975	46·08	33·11
0·015234 *	0·88015	2·2910	2·2571	46·39	33·40

${}_{\infty}P_{\mathrm{T}} = 46{\cdot}14$ c.c.; $P_{\mathrm{E}} = 33{\cdot}00$ c.c.; $P_{\mathrm{O}} = 13{\cdot}14$ c.c.; whence $\mu = 0{\cdot}80$ D.

1 : 4-*Dioxatetralin.*

f_2.	d_s.	ε.	n^2.	P_2.	${}_{\mathrm{E}}P_2$.
0·049170	0·8916	2·41760	2·26732	79·62	37·28
0·038923	0·8889	2·39341	2·26647	79·13	37·66
0·030757	0·8860	2·37005	2·26439	79·97	37·38
0·029209 *	0·88680	2·366	2·2627	78·23	36·63
0·025326	0·8840	2·35228	2·26303	79·64	37·23
0·019682	0·8818	2·33496	2·26179	77·88	37·15
0·016754	0·8807	2·32610	2·26117	80·16	37·06
0·015337 *	0·88112	2·324	2·2594	78·70	36·35

${}_{\infty}P_{\mathrm{T}} = 79{\cdot}40$ c.c.; $P_{\mathrm{E}} = 37{\cdot}29$ c.c.; $P_{\mathrm{O}} = 42{\cdot}11$; whence $\mu = 1{\cdot}42$ D.

5-*Nitro*-1 : 3-*dioxaindane.*

f_2.	d_s.	ε.	n^2.	P_2.	${}_{\mathrm{E}}P_2$.
0·014598	0·8830	2·75825	2·26245	482·56	42·77
0·011286	0·8808	2·64731	2·26102	487·90	42·66
0·008203	0·8787	2·54561	2·26008	499·41	43·73
0·005425	0·8771	2·46001	2·25905	524·86	43·19

${}_{\infty}P_{\mathrm{T}} = 521{\cdot}00$ c.c.; $P_{\mathrm{E}} = 43{\cdot}09$ c.c.; $P_{\mathrm{O}} = 477{\cdot}91$ c.c.; whence $\mu = 4{\cdot}80$ D.

6-*Nitro*-1 : 4-*dioxatetralin.*

f_2.	d_s.	ε.	n^2.	P_2.	${}_{\mathrm{E}}P_2$.
0·013932	0·8830	2·89408	2·26392	617·28	48·21
0·012049	0·8816	2·80219	2·26297	619·67	48·67
0·008198	0·8792	2·63524	2·26119	642·46	48·43
0·005860	0·8776	2·51923	2·26015	627·32	48·96
0·003814	0·8762	2·4381	2·25920	656·64	49·91

${}_{\infty}P_{\mathrm{T}} = 652{\cdot}5$ c.c.; $P_{\mathrm{E}} = 48{\cdot}84$ c.c.; $P_{\mathrm{O}} = 603{\cdot}66$ c.c.; whence $\mu = 5{\cdot}40$ D.

5 : 6-*Dibromo*-1 : 3-*dioxaindane.*

f_2.	d_s.	ε.	n^2.	P_2.	${}_{\mathrm{E}}P_2$.
0·029396	0·9264	2·5659	2·76702	179·00	44·78
0·021774	0·9128	2·4894	2·76441	180·78	44·85
0·020435	0·9103	2·47512	2·26400	180·48	44·90
0·016194	0·9026	2·43252	2·26255	181·66	45·48
0·015857	0·9020	2·43004	2·26242	182·45	45·43
0·009491	0·8905	2·36751	2·26031	185·54	46·01

${}_{\infty}P_{\mathrm{T}} = 186{\cdot}50$ c.c.; $P_{\mathrm{E}} = 45{\cdot}24$ c.c.; $P_{\mathrm{O}} = 141{\cdot}26$ c.c.; whence $\mu = 2{\cdot}61$ D.

6 : 7-*Dibromo*-1 : 4-*dioxatetralin.*

f_2.	d_s.	ε.	n^2.	P_2.	${}_{\mathrm{E}}P_2$.
0·021805	0·9137	2·7237	2·26622	322·48	49·62
0·013933	0·8994	2·5616	2·26300	331·44	49·73
0·013390	0·8983	2·55008	2·26272	332·00	49·85
0·010562	0·8929	2·4912	2·26155	335·69	50·61
0·008435	0·8894	2·44223	2·26065	330·37	49·42
0·007653	0·8877	2·42734	2·26030	332·22	50·33

${}_{\infty}P_{\mathrm{T}} = 332{\cdot}34$ c.c.; $P_{\mathrm{E}} = 49{\cdot}59$ c.c.; $P_{\mathrm{O}} = 282{\cdot}75$ c.c.; whence $\mu = 4{\cdot}00$ D.

* Results obtained in Manchester (1948).

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DYSON PERRINS LABORATORY, OXFORD.
THE UNIVERSITY OF MANCHESTER.

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