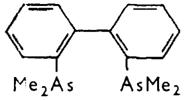
527. *Cyclic Diarsines. Part VII.*[1] *The Optical Resolution of Some Cyclic Quaternary Diarsonium Dibromides.*

By M. H. Forbes, Frederick G. Mann, Ian T. Millar,
and E. A. Moelwyn-Hughes.

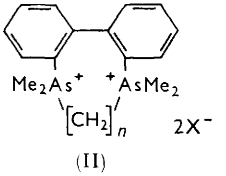
The series of four diarsonium dibromides, (II; $n = 1$, 2, or 3; X = Br) and (III; X = Br), consist of a biphenyl nucleus 2,2′-linked, as shown, to form a central 7-, 8-, 9-, and 10-membered diarsonium ring, respectively. The four dibromides have been resolved into optically active forms, having $[M]_D$ +174°, −179°; +306°, −307°; +487°, −501°; and +557°, −560°, respectively.

The first of these salts racemises comparatively readily in aqueous solution, the second more slowly, and the remaining salts did not racemise at 150°.

Part V[2] of this series described an improved preparation of 2,2′-biphenylylenebisdimethylarsine (I), which was combined with methylene, trimethylene, and *o*-xylylene dibromide to give the cyclic diarsonium dibromides (II; $n = 1$ or 3; X = Br) and (III; X = Br), respectively; the combination with ethylene dibromide to give the dibromide (II; $n = 2$; X = Br) had been earlier recorded.[3] The thermal decomposition of these four dibromides and of the dihydroxides (II; $n = 1$, 2, or 3; X = OH) has also been described.[2,3]



(I)



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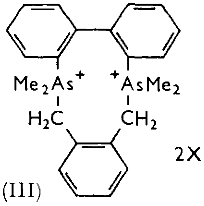
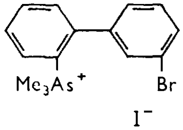


(III)



(IV)

Since the heterocyclic ring systems in the dibromides (II; $n = 1$, 2, or 3; X = Br) and (III; X = Br) force the two *o*-phenylene groups out of coplanarity, the salts should be susceptible to optical resolution. Indeed, there is little doubt that the dimethobromide of the diarsine (I) should also be resolvable, for Lesslie and Turner[4] have effected the partial resolution of the methiodide (IV) of 3′-bromo-2-dimethylarsinobiphenyl. It is noteworthy that the ultraviolet spectra of the dimethiodide of the diarsine (I) and of the dibromides (II; $n = 1$, 2, or 3; X = Br) and (III; X = Br) show no evidence of the typical strong band at *ca.* 250 mμ of an unrestricted biphenyl molecule, although that of the dibromide (II; $n = 1$, X = Br) does show exceptionally a band at 238 mμ (ε 6500) which may be the displaced biphenyl band.[1] Similar values for this band are shown by 2-methylbiphenyl (237 mμ; ε 10,500) and 2-ethylbiphenyl (233 mμ; 9000), but the band is missing in the spectrum of 2,2′-dimethylbiphenyl.[5]

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[1] Part VI, M. H. Forbes, Heinekey, Mann, and Millar, *J.*, 1961, 2762.
[2] Heaney, Heinekey, Mann, and Millar, *J.*, 1958, 3838.
[3] Heaney, Mann, and Millar, *J.*, 1957, 3930.
[4] Lesslie and Turner, *J.*, 1933, 1588.
[5] Braude, Sondheimer, and W. F. Forbes, *Nature*, 1954, **173**, 117.

In our resolution experiments, the dibromide (II; $n = 1$; X = Br) was converted into the (+)-tartrate, the di[hydrogen (—)-dibenzoyltartrate] and the di-[(—)-menthyloxyacetate], all of which were intractable hygroscopic gums: recrystallisation of the di-(+)-α-bromocamphorsulphonate from ethanol gave, however, evidence of partial resolution and racemisation of the cation. Ultimately it was found that the diastereoisomeric (+)-dibenzoyltartrates (II; $n = 2$; X = $C_{18}H_{12}O_8$) had markedly different solubilities in cold acetonitrile: the crude mixture was therefore repeatedly extracted with acetonitrile at room temperature until the residue had a constant rotation of [α] +85·2° in aqueous solution. An aqueous solution of this salt was then passed down an ion-exchange column of Amberlite IRA-400 which had previously been converted into the bromide: the eluate when concentrated under reduced pressure and finally freeze-dried gave the crystalline (+)-dibromide, $[M]_D$ +174°. Repetition of this experiment with the (—)-dibenzoyltartrate gave a residue having $[\alpha]_D$ —82·8°, which in turn furnished the (—)-dibromide, $[M]_D$ —179°.

The dibromide (II; $n = 2$; X = Br) was converted into the di-(+)α-bromocamphorsulphonate, which after ten recrystallisations from ethanol had a constant rotation $[M]_D$ +862° in aqueous solution; this solution, when passed down the column as before, gave the optically pure (+)-dibromide, $[M]_D$ +306°. The di-(—)-α-bromocamphorsulphonate when similarly treated afforded the (—)-dibromide, $[M]_D$ —307°. It is noteworthy that recrystallisation of the di-(+)-camphorsulphonate gave no evidence of resolution.

The dibromide (II; $n = 3$; X = Br) was also converted into the di-(+)-α-dibromocamphorsulphonate, which after recrystallisation from ethanol until it had a constant rotation was converted into the optically pure (+)-dibromide having $[M]_D$ +487° in aqueous solution. The di-(—)-α-bromocamphorsulphonate similarly gave the (—)-dibromide, $[M]_D$ —501°.

Resolution of the dibromide (III; X = Br) initially proved troublesome. It was converted into the di-(+)-α-bromocamphorsulphonate, which at first could not be recrystallised: repeated extraction with cold acetonitrile, however, gave considerable although incomplete resolution. This product could now be recrystallised from water, and had finally $[M]_D$ +1110° in aqueous solution. It was converted into the optically pure (+)-dibromide, $[M]_D$ +557°. The di-(—)-α-bromocamphorsulphonate could now with care be fractionally recrystallised from water until it had $[M]_D$ —1100°, and then furnished the (—)-dibromide, $[M]_D$ —560°.

It is noteworthy that the molecular rotations of the four dibromides, (II; $n = 1$, 2, or 3; X = Br) and (III; X = Br), increase steadily in this order, *i.e.*, with increasing size of the central heterocyclic ring.

The stereochemical characteristics of many compounds having a biphenyl nucleus linked across the 2,2′-positions by bridges of various types and sizes have been elucidated, and some generalisations correlating the nature of the bridge and the optical stability of the compound have been suggested. For example, if the bridge consists of 3 or 4 atoms, the compound will have low optical stability unless the biphenyl nucleus carries substituents in the 6,6′-positions:[6] also, biphenyls with such bridges are optically less stable than unbridged compounds with similar blocking groups, and a biphenyl with a 3-membered bridge is less stable than an analogous biphenyl with a 4-membered bridge when both have the same 6,6′-substituents.[7]

The diarsonium salts (II; $n = 1$, 2, or 3; X = Br) and (III; X = Br) form a unique series in that the bridge has two heteroatoms directly linked to the biphenyl nucleus, the first three compounds, moreover, forming a homologous series.

The above generalisations cannot therefore be satisfactorily applied to our salts, particularly as our attempts to resolve the dimethiodide of the diarsine (I) have failed.

[6] Iffland and Siegel, *J. Org. Chem.*, 1956, **21**, 1056; Trace and Emrick, *J. Amer. Chem. Soc.*, 1956, **78**, 6130; Dvorken, Smyth, and Mislow, *ibid.*, 1958, **80**, 486.

[7] Ahmed and Hall, *J.*, 1959, 3383.

The three salts (II; $n = 1$, 2, or 3; X = Br) do, however, show an increase in optical stability as the length of the bridge increases.

Thus an aqueous solution of the (+)-dibromide (II; $n = 1$; X = Br) kept at room temperature retained some of its activity after four weeks: the activity of a 0·553% solution at 33·5° fell from [α] +30·25° to 8·14° in 90 hours, and that of a 0·814% solution at 70° fell from [α] +29·5° to +3·07° in 2 hours.

An aqueous solution of the (+)-dibromide (II; $n = 2$; X = Br) kept at room temperature retained its activity unimpaired for several months; the activity of a 0·704% solution in a sealed tube at 100° fell from [α] +50·8° to +5·00° in 60 hours, and that of a 0·4167% solution at 150° fell from [α] +50·8° to +4·00° in 50 minutes.

In constrast, aqueous solutions of the dibromides (II; $n = 3$; X = Br) and (III; X = Br) were kept in sealed tubes at 150° for 3 hours without perceptible change in activity.

In view of these results, it is significant that only the most readily racemised dibromide (II; $n = 1$; X = Br) showed an apparent biphenyl band in its ultraviolet absorption spectrum.

Racemisation Rates of the Dibromide (II; $n = 1$; X = Br).—Rotations were measured as before for $\mathrm{Na_D}$ light, but with a 1 dm. tube. A 3·300% aqueous solution of the (+)dibromide trihydrate had α +0·731°, [α] +22·15°: a 3·350% solution of the (—)-salt had α —0·791°, [α] —23·6°. (The low values of [α] may indicate the effect of the higher concentration on the rotatory power, or possibly a partial racemisation of the salts while stored for 10 months at room temperature.)

Three kinetic runs were carried out. The first was made on the solution (0·6 ml.) in the polarimeter tube kept at 25·0°. For the second and the third run, at 48·69° and 61·82°, respectively, 5 samples of the solution (*ca.* 0·7 ml. each) were sealed in Pyrex tubes, placed in the thermostat-bath, and removed at known times, chilled in ice, and transferred to the polarimeter tube. Solutions of the (—)-salt were used for the first two runs, and that of the (+)-salt for the third run.

The results at 62·82° (Table 1), when plotted logarithmically, give a mean value of $k_1 = 1{\cdot}536 \times 10^{-4}$ sec.$^{-1}$, where $k_1 = (1/t) \ln (\alpha_0/\alpha_t)$: the mean of the separate values calculated for k_1 is $1{\cdot}540 \times 10^{-4}$ sec.$^{-1}$.

TABLE 1.

Racemisation of a 3·300% aqueous solution of the (+)-dibromide at 335·98°K.

t (min.)	0	50	90	130	170
α, obs.	0·708°	0·450°	0·300°	0·214°	0·149°
calc.	0·708°	0·447°	0·309°	0·214°	0·148°
$10^4 k_1$ (sec.$^{-1}$)	—	1·51	1·59	1·53	1·53

TABLE 2.

Unimolecular constants at various temperatures.

Temp. (K)	298·17°	321·85°	335·98°
$10^6 k_1$ (sec.$^{-1}$): obs.	1·08	30·8	153·6
calc.	1·087	30·65	153·2

Unimolecular constants (Table 2) were similarly determined at 25·0° and 48·69°. If they are cast in the form $k_1 = A \exp(-E_A/\boldsymbol{R}T)$, then $\log_{10} A$ (sec.$^{-1}$) = $13{\cdot}04 \pm 0{\cdot}03$ and E_A (kcal./mole) = $25{\cdot}9 \pm 1{\cdot}3$. If they are inserted in the equation $k_1 = (\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta H^{\ddagger}/\boldsymbol{R}T) \exp(\Delta S^{\ddagger}/\boldsymbol{R})$,[8] then $\Delta H^{\ddagger}$ (kcal./mole) = $25{\cdot}3 \pm 1{\cdot}3$, and

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[8] Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill, New York, 1941.

$\Delta S^{\ddagger} = -0{\cdot}98$ cal. mole^{-1} degree^{-1}.[9] Neither of these equations reproduces the data as well as the empirical equation $\log_{10} k_1 = 202{\cdot}2 - 64{\cdot}41 \log_{10} T - 14{,}550/T$ (Table 2), according to which $E_A = \boldsymbol{R}T^2(\mathrm{d}\ln k_1/\mathrm{d}T) = 66{\cdot}500 - 128T$ (cal./mole). The coefficient of T is uncertain to ±20%.[10]

A detailed investigation of the racemisation of the dibromide (II; $n = 2$; X = Br) was not carried out.

EXPERIMENTAL

All compounds were colourless unless otherwise stated. The m. p.s of the quaternary arsonium salts were determined in sealed, evacuated, capillary tubes. Optical rotations, unless otherwise indicated, were measured for aqueous solutions at 20—23° in a Rudolph photoelectric spectropolarimeter, with a 2 dm. polarimeter tube and Na$_D$ light (λ 5893 Å).

The diarsonium dibromides (II; $n = 1$, 2, or 3; X = Br) usually crystallise as polyhydrates (often trihydrates), which when confined in a vacuum-desiccator tend to fall in clear stages to lower hydrates, and when heated under reduced pressure give the anhydrous salts. The optically active dibromides were therefore analysed at the time of the rotation measurements to determine the particular hydrate isolated.

Ion-exchange Column.—This was packed with Amberlite IRA-400 resin, having the NMe$_3^+$ groups neutralised by Cl$^-$ ions. The column was first subjected to prolonged treatment with 5% aqueous sodium hydroxide until the eluate was free from halide, and then with water to remove the excess of hydroxide. 5% Aqueous sodium bromide was passed down until the eluate was neutral, this being followed by thorough treatment with water to remove any excess of sodium bromide. This process was always employed to ensure complete conversion of the resin into the bromide salt.

5,5,7,7-*Tetramethyl*-5,7-*diarsonia*-1,2:3,4-*dibenzocycloheptadiene Dibromide* (II; $n = 1$; X = Br).—A mixture of the diarsine (I) (7·243 g.), methanol (10 ml.), and methylene dibromide (3·477 g., 1 mol.) in a pressure-bottle was slowly heated to 100° and kept at this temperature for 10 hr. The cold, almost solid product was collected, washed with methanol, and recrystallised from ethanol–light petroleum (b. p. 60—80°), giving the dibromide (6·63 g., 61%), m. p. 223—226° (lit.,[2] 224—225°).

Resolution. A solution of the (±)dibromide (2·304 g.) in water (25 ml.) was run slowly into a stirred suspension of disilver (+)-dibenzoyltartrate (2·601 g., 1 mol.) in hot water (250 ml.); as silver bromide was precipitated, the disilver salt dissolved. The hot mixture was digested for 10 min., then filtered, and the filtrate concentrated at 15 mm., again filtered, cooled, and freeze-dried in a high vacuum, leaving a crystalline deposit. Acetonitrile (20—25 ml.) and 50 glass beads of *ca.* 0·4 mm. diameter were added, and the mixture was vigorously shaken. The undissolved material became at first slightly sticky, then hardened, and finally gave a fine suspension. This was transferred to a centrifuge tube, and after centrifugation, the supernatant liquid was decanted, and the residue mixed with small portions of acetonitrile so that it could be completely returned by a pipette to the flask containing the beads. After 10 such extractions, the deposit was centrifuged with ether, collected, and dried; a 0·581% solution had α +1·025°, [α] +88·2°. The deposit was extracted twice more with acetonitrile, giving the (+)-*diarsonium* (+)-*dibenzoyltartrate trihydrate* (II; $n = 1$; X = $C_{18}H_{12}O_8$), m. p. 174—175° (Found: C, 52·6; H, 5·1. $C_{35}H_{34}As_2O_8,3H_2O$ requires C, 53·5; H, 5·4%); a 0·394% solution had α +0·695°, [α] +88·15°.

An aqueous solution of this salt (0·534 g.) was passed down the column, and the clear eluate concentrated in a rotatory evaporator at 12 mm. and finally freeze-dried. The fine crystals, when dried at 0·2 mm. at room temperature, afforded the (+)-*dibromide trihydrate* (II; $n = 1$; X = Br) (0·392 g.), m. p. 228° (Found: C, 34·4; H, 4·6. $C_{17}H_{22}As_2Br_2,3H_2O$ requires C, 34·6; H, 4·8%). A 0·814% solution had α +0·480°, [α] +29 5°, [M] +174°.

The (±)-dibromide (II; $n = 2$; X = Br) (2·241 g.) was similarly treated with disilver (—)-dibenzoyltartrate (2·533 g., 1 mol.), and the crystalline deposit, when extracted ten times as before with cold acetonitrile, gave the (—)-*diarsonium* (—)-*dibenzoyltartrate trihydrate*; a

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[9] For a tabulation of similar values for many substituted biphenyls, see Hall and Harris, *J.*, 1960, 490.

[10] For other examples of similar ranges, see Moelwyn-Hughes, "The Kinetics of Reactions in Solution," The Clarendon Press, Oxford, 2nd edn., 1947, p. 58.

0·528% solution (*l*, 1 dm.) had α −0·435°, [α] −82·4°. Five more extractions gave the optically pure salt, m. p. 174° (Found: C, 53·6; H, 5·6%), a 0·338% solution (*l*, 1 dm.) having α −0·280°, [α] −82·8°.

This salt was converted as before into the (−)-*dibromide trihydrate* (II; *n* = 1; X = Br), m. p. 228—229° (Found: C, 34·7; H, 5·0%); a 0·388% solution had α −0·235°, [α] −30·3°, [*M*] −179°.

The (±)-dibromide was similarly converted into the *di-*(+)*-α-bromocamphorsulphonate monohydrate*, m. p. 276—280° (Found: C, 43·9; H, 5·3. $C_{37}H_{50}As_2Br_2O_8S_2,H_2O$ requires C, 44·1; H, 5·2%); after 2 and 3 recrystallisations from ethanol, the salt in water had [*M*] +690° and +587°, respectively; since the (+)-bromocamphorsulphonate ion has [*M*] +278° in water, partial resolution had occurred but the cation was rapidly racemising during recrystallisation.

5,5,8,8-*Tetramethyl*-5,8-*diarsonia*-1,2:3,4-*dibenzocyclo-octadiene Dibromide* (II; *n* = 2; X = Br).—A mixture of the diarsine (I) (14·486 g.), ethylene dibromide (7·515 g., 1 mol.), and methanol (20 ml.) was heated in a pressure-bottle at 100° for 16 hr. The cold powdered crystalline mass, when recrystallised from ethanol–light petroleum (b. p. 60—80°), gave the dibromide (20·28 g., 92%), m. p. 206—208° (lit.,[1] 211—213°).

Resolution. A solution of the dibromide (2·914 g.) in water (20 ml.) was added to a hot stirred solution of silver di-(+)-bromocamphorsulphonate (4·474 g., 2 mol.) in water (100 ml.). After 10 min., the mixture was cooled and filtered; the filtrate was evaporated at 15 mm. to dryness. After 4 and 6 recrystallisations from ethanol, the salt had [*M*] +845° and +868°, respectively; after 10 recrystallisations, a 1·890% solution of the *diarsonium* (+)*-dibromocamphorsulphonate* (II; *n* = 2; X = $C_{10}H_{14}BrO_4S$) had α +3·228°, [*M*] +862° (Found, after drying at 100°/0·1 mm.: C, 45·0; H, 5·2. $C_{38}H_{52}As_2Br_2O_8S_2$ requires C, 45·2; H, 5·2%).

An aqueous solution of the last fraction of the di-sulphonate (0·189 g.), when passed down the column, then evaporated to dryness, and finally freeze-dried, afforded the (+)*-diarsonium dibromide trihydrate* (II; *n* = 2; X = Br) (0·1033 g.), m. p. 226—228° after drying at 15°/0·2 mm. (Found: C, 35·5; H, 5·4%); a 0·799% solution of the salt had α +0·810°, [α] +50·7°, [*M*] +306°.

The (±)-dibromide was similarly converted by silver (−)-bromocamphorsulphonate into the di-(−)-bromocamphorsulphonate, m. p. 283° after 4 recrystallisations from ethanol; after 6 it had [*M*] −862°, and after 7 recrystallisations a 1·093% solution had α −1·861°, [*M*] −859°.

This salt afforded the (−)*-dibromide trihydrate*, m. p. 229° (Found: C, 35·7; H, 5·0. $C_{18}H_{24}As_2Br_2,3H_2O$ requires C, 35·8; H, 5·0%); a 0·7040% solution had α −0·715°, [α] −50·8°, [*M*] −307°.

The (±)-dibromide was also converted into the *di-*(+)*-camphorsulphonate* (II; *n* = 2; X = $C_{10}H_{15}O_4S$), which could not be crystallised from the common solvents: after 8 recrystallisations from ethanol–light petroleum (b. p. 60—80°) (1 : 4 v/v) it had m. p. 222—227° with preliminary softening (Found: C, 51·8; H, 6·3. $C_{38}H_{54}As_2O_8S_2,1\frac{1}{2}H_2O$ requires C, 51·9; H, 6·5%). Since it was isomerically impure, it was not further investigated.

5,5,9,9-*Tetramethyl*-5,9-*diarsonia*-1,2:3,4-*dibenzocyclononadiene Dibromide* (II; *n* = 3; X = Br).—This salt was prepared by the interaction of the diarsine (I) (14·50 g.) and trimethylene dibromide (8·07 g., 1 mol.) in methanol (30 ml.) at 100° for 6 hr. The cold semi-solid contents of the pressure-bottle were heated with methanol (50 ml.) to give a clear solution, which when cooled and stirred deposited the dibromide (6·213 g., 28%), m. p. 260—261° (effervescence) (lit.,[1] 261—262°). Concentration of the filtrate gave a much larger second crop.

Resolution. Solutions of the dibromide (12·006 g.) and silver (+)-α-bromocamphorsulphonate (18·103 g., 2 mol.) in water (125 and 100 ml.) were mixed, digested briefly at 100°, filtered, and evaporated as before. The (+)*-diarsonium* (+)*-di-α-bromocamphorsulphonate* (II; *n* = 3; X = $C_{10}H_{14}BrO_4S$) had m. p. 286—288° after 4 recrystallisations from ethanol; after 5 it had [*M*] +1047°, and after 6 recrystallisations it had α +2·104°, [*M*] +1042° in a 1·036% solution (Found, after drying at 100°/0·2 mm.: C, 45·8; H, 5·4. $C_{39}H_{54}As_2Br_2O_8S_2$ requires C, 45·7; H, 5·3%).

This salt was converted into the (+)*-dibromide monohydrate* (II; *n* = 3; X = Br), m. p. 240° after drying at 15°/0·2 mm. (Found: C, 39·3; H, 4·7. $C_{19}H_{26}As_2Br_2,H_2O$ requires C, 39·2; H, 4·9%); a 1·354% solution (*l*, 1 dm.) had α +1·130°, [*M*] +485°.

The mother-liquors from the recrystallisation of the di-(+)-bromocamphorsulphonate were united, concentrated, and added to hot saturated aqueous sodium iodide. The precipitated di-iodide (II; $n = 3$; X = I), m. p. 254—256°, rich in the (−)-form, was collected from the cold product, washed with water, dried, and converted into the *di-(−)-bromocamphorsulphonate*, which after 3 recrystallisations from ethanol had m. p. 290°, [*M*] −1042° in water; after 4 recrystallisations it had α −3·365°, [*M*] −1050° in 1·640% solution.

This salt in aqueous solution was converted into the *(−)-dibromide monohydrate*, m. p. 241° after drying at 15°/0·2 mm. (Found: C, 39·5; H, 5·1%); a 1·272% solution (*l*, 1 dm.) had α −1·095°, [*M*] −501°.

5,5,10,10-*Tetramethyl*-5,10-*diarsonia*-1,2:3,4:7,8-*tribenzocyclodecatriene Dibromide* (III; X = Br).—A mixture of the diarsine (I) (4·5636 g.), *o*-xylylene dibromide (3·8604 g., 1 mol.), and methanol (30 ml.) was heated under reflux on a steam-bath for 6 hr., and the clear solution then evaporated to dryness. Careful recrystallisation of the pale brown residue from ethanol gave the dibromide (III; X = Br), m. p. 209° (lit.,[1] 209—210°).

Resolution. Solutions of the dibromide (1·3030 g.) and of silver (+)-bromocamphorsulphonate (1·6999 g., 2 mol.) in hot water (25 and 100 ml.) were mixed, heated briefly at 100°, filtered, concentrated, and freeze-dried, giving the *(±)-diarsonium di-(+)-bromocamphorsulphonate monohydrate*, m. p. 275—281°. A portion of this salt was recrystallised from ethanol without providing evidence of resolution (Found: C, 47·8; H, 5·0. $C_{44}H_{58}As_2Br_2O_8S_2,H_2O$ requires C, 47·8; H, 5·3%). Since crystallisation from other solvents was unsatisfactory, the powdered salt was extracted with cold acetonitrile as previously described: the salt, after 3, 8, 10, 11, and 12 extractions, had [α] +62·2°, 93·0°, 95·0°, 94·1°, and 94·7°, respectively, in aqueous solution. This material could now be recrystallised from water, and after 1 recrystallisation had [α] +103·4°: 3 recrystallisations furnished the pure (+)-diarsonium di-(+)-bromocamphorsulphonate (III; X = $C_{10}H_{14}BrO_4S$), m. p. 288°, a 0·461% solution having α +0·945°, [α] +103°, [*M*] +1110°.

An aqueous solution of this salt, when passed down the column and then evaporated, gave the *(+)-dibromide dihydrate* (III; X = Br), m. p. 185—187° (Found: C, 43·4; H, 5·2. $C_{24}H_{28}As_2Br_2,2H_2O$ requires C, 43·5; H, 4·9%); a 0·889% solution had α +1·495°, [*M*] +557°.

The (±)-diarsonium di-(−)-bromocamphorsulphonate was similarly prepared. A concentrated aqueous solution, when set aside overnight, deposited an oil: the mixture was heated to redissolve the oil, boiled with activated charcoal, filtered hot through "Supercel" and concentrated under reduced pressure on the steam-bath, a considerable amount of crystals separating meanwhile. Seven recrystallisations from water gave the *(−)-diarsonium di-(−)-bromocamphorsulphonate* (III; X = $C_{10}H_{14}BrO_4S$); a 0·915% solution had α −1·870°, [α] −102·2°, [*M*] −1109°.

This salt, when passed in aqueous solution down the column, afforded the *(−)-dibromide trihydrate*, m. p. 189—190° (Found: C, 42·3; H, 5·5. $C_{24}H_{28}As_2Br_2,3H_2O$ requires C, 42·4; H, 5·1%); a 0·589% solution had α −0·970°, [*M*] −560°.

The (±)-dibromide (III; X = Br) was also converted into the *di-(+)-camphorsulphonate monohydrate* (III; X = $C_{10}H_{15}O_4S$), m. p. 250—260° (Found: C, 56·2; H, 6·7. $C_{44}H_{58}As_2O_8S_2,H_2O$ requires C, 55·8; H, 6·4%), but showed no evidence of resolution.

Dimethiodide of the Diarsine (I).—This salt was prepared as described earlier.[1] To investigate its optical resolution, it was converted into the di-(+)-camphorsulphonate, the di-(+)-bromocamphorsulphonate, the (+)-tartrate, the (+)-dibenzoyltartrate, and the di-(−)-menthyloxyacetate, but very unsatisfactory products were always obtained.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.
THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KEELE, STAFFORDSHIRE.

[*Received, December 12th, 1962.*]