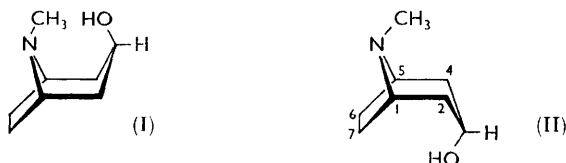


### 784. Molecular Polarisability: The Conformations of Tropinone and 3-Halogenotropanes as Solutes in Benzene.

By J. M. ECKERT and R. J. W. LE FÈVRE.

Dipole moments, molar Kerr constants, refractivities, etc., are reported for tropine, tropinone, and 3-chloro- and 3-bromo-tropine. Comparisons of values for  $\mu$  and  $\infty(mK_2)$  from experiment with those calculated, from bond moment and polarisability data, for rival space formulæ indicate that chair piperidine rings with equatorially disposed *N*-methyl groups are contained in the preferred solute conformations.

CHEMICAL evidence on the conformation of the piperidine ring in tropine and its epimer <sup>1</sup> is inconclusive. Fodor and Nador <sup>2</sup> considered that stereospecific migrations of acyl groups from nitrogen to oxygen indicated the relative positions of the O-H and N-H bonds in nor- $\psi$ -tropine and nor-tropine, and therefore, by analogy, in the related *N*-methyl derivatives,  $\psi$ -tropine and tropine. The demonstration by Hardegger and Ott <sup>3</sup> that nor- $\psi$ -tropine, but not nortropine, could give a cyclic condensation product in which the oxygen and the nitrogen atom were united by a bridge, the observation <sup>4</sup> of spectral signs of intramolecular hydrogen bonding in  $\psi$ -tropine, the dipole moments <sup>4,5</sup> of tropine and  $\psi$ -tropine, and the higher p*K* value <sup>6</sup> of the  $\psi$ -isomer, all seemed consistent with formula (I) for  $\psi$ -tropine. Paddock,<sup>7</sup> however, argued that  $\psi$ -tropine, produced <sup>8</sup> by reduction of tropinone with lithium aluminium hydride, should possess a C-O bond disposed parallel to the bonds between carbons 1 and 2, or 4 and 5 [*i.e.*, with H and OH interchanged in (I)], and that on this basis the slower hydrolysis <sup>9</sup> of esters of tropine was attributable to steric hindrance by the NMe group. Sparke <sup>10</sup> criticised Paddock's view, and favoured the proposal of Bose and Chaudhuri <sup>11</sup> that the piperidine ring in both tropine and  $\psi$ -tropine



has a "chair" conformation (II), with the hydroxyl group attached respectively axially or equatorially in the two isomers, so that the kinetic differences noted for the hydrolysis of tropine and  $\psi$ -tropine esters were those usually expected with axial and equatorial substituents in cyclohexane and related ring systems. Firm physical evidence for the first time was provided by the report by Visser *et al.*<sup>12</sup> that an *X*-ray analysis of tropine hydrobromide agreed with a "trans-chair" form for tropine. Archer and Lewis<sup>13</sup>

<sup>1</sup> Willstätter, *Ber.*, 1896, **29**, 936; Willstätter and Bode, *Ber.*, 1900, **33**, 416; Willstätter and Bommer, *Annalen*, 1921, **422**, 18; Barrowcliff and Tutin, *J.*, 1909, **95**, 1967.

<sup>2</sup> Fodor and Nador, *Nature*, 1952, **169**, 462; *J.*, 1953, 721; cf. Fieser and Nickson, *J. Amer. Chem. Soc.*, 1952, **74**, 5566.

<sup>3</sup> Hardegger and Ott, *Helv. Chim. Acta*, 1953, **36**, 1186.

<sup>4</sup> Zenitz, Martini, Priznar, and Nachod, *J. Amer. Chem. Soc.*, 1952, **74**, 5364.

<sup>5</sup> Clemo and Jack, *Chem. and Ind.*, 1953, 195.

<sup>6</sup> Smith and Hartung, *J. Amer. Chem. Soc.*, 1953, **75**, 3859.

<sup>7</sup> Paddock, *Chem. and Ind.*, 1953, 63.

<sup>8</sup> Mirza, *Nature*, 1952, **170**, 630.

<sup>9</sup> Sixma, Siegmann, and Beyermann, *Proc. K. Ned. Acad. Wet.*, 1951, **54**, B, 452.

<sup>10</sup> Sparke, *Chem. and Ind.*, 1953, 749.

<sup>11</sup> Bose and Chaudhuri, *Nature*, 1953, **171**, 652.

<sup>12</sup> Visser, Manassen, and de Vries, *Acta Cryst.*, 1954, **7**, 288.

<sup>13</sup> Archer and Lewis, *Chem. and Ind.*, 1954, 853.

reconciled a "cis-chair" (having an equatorial hydroxyl group) with the chemical observations in refs. 2—6 by suggesting that the  $\psi$ -isomer exists at best partially as, or can easily pass into, the "boat" form (I). Fodor<sup>14</sup> in his 1955 review accepts as probable that  $\psi$ -tropine in its ground state is mainly in a chair conformation, but that an "equilibrium between boat and chair conformations takes place whenever heat energy is transferred to the system." Tropine itself is therefore also a chair structure, holding hydroxyl axially.

The disposition of the *N*-methyl group is another problem. Fodor,<sup>14</sup> arguing that quaternisation of the tropane nitrogen occurs with marked stereospecificity, the second alkyl always entering equatorially, represented tropine as (II); additionally, form (II) would avoid steric compressions possible between the ethylene bridge and an equatorially attached *N*-Me group. Closs<sup>15</sup> has recently questioned the first of these deductions on kinetic grounds.

Closs states that his nuclear magnetic resonance studies on the deuterohalides of a series of tropane derivatives are compatible with equatorial rather than axial arrangements, for the former of which, he adds, models indicate that there is negligible strain.

Against this background we noted that preliminary calculations of the anisotropic polarisabilities expected for tropinone depended upon whether the piperidone ring was taken as a boat or a chair form. Since a common skeletal configuration for tropine,  $\psi$ -tropine, and tropinone is not disputed, a decision on the ring system in the last-named should assist recognition of either (I) or (II) as the correct framework for the epimeric tropines. Measurements of the molar Kerr constant and dipole moment of tropinone as a solute in benzene have therefore been made, and are here reported, together with others on 3-chloro- and 3-bromo-tropane (from which the conformation of the *N*-Me bond may be inferred) and tropine (for the dipole moment of which there is disagreement in the literature).

## EXPERIMENTAL

*General.*—Apparatus, procedures, notation, and methods of calculation are described in refs. 16 and 17; symbols and equations required for the treatment of observational data have recently<sup>18</sup> been summarised in this *Journal*.

*Solvent.*—The solvent used was freshly distilled sodium-dried benzene,  $\epsilon^{25}$  2.2725,  $d_4^{25}$  0.87378,  $n_D^{25}$  1.4973,  $10^7 E_D^{25}$  0.410.

*Solutes.*—Commercial samples of tropine and tropinone (from Fluka, Switzerland) were recrystallised to constant m. p. (61—63° and 40—42°, respectively). The hydrohalides of 3-chloro- and 3-bromo-tropane were prepared by heating tropine with the corresponding concentrated acid in a sealed tube.<sup>19</sup> Recrystallisation from alcohol yielded solids, m. p. 235—238° and 210—215°, respectively; from these, the required halogenotropanes were obtained, as colourless oils, by treating aqueous solutions with alkali.

*Measurements.*—These are listed in Table 1; quantities calculated therefrom, including dipole moments and molar Kerr constants at infinite dilution, are in Table 2. At the weight-fractions  $w_2$  used, the differences  $\Delta n$  between the refractive indexes of solutions and solvent were beneath detection with all four solutes; for tropine, the analogous differences  $\Delta B$  between the Kerr constants were less than  $0.001 \times 10^{-7}$ .

*Previous Determinations.*—Conflicting dipole moments have been recorded for tropine by Zenitz *et al.*<sup>4</sup> (1.59 D) and by Clemo and Jack<sup>5</sup> (<0.4 D). The present value (1.55 D) agrees,

<sup>14</sup> Fodor, *Acta. Chim. Acad. Sci. Hung.*, 1955, **5**, 379.

<sup>15</sup> Closs, *J. Amer. Chem. Soc.*, 1959, **81**, 5456.

<sup>16</sup> Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (b) *J.*, 1953, 4041; (c) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., Vol. I, p. 2459; (d) *J.*, 1956, 3549.

<sup>17</sup> Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. 2.

<sup>18</sup> Le Fèvre and Sundaram, *J.*, 1962, 1494.

<sup>19</sup> Polonovski and Polonovski, *Bull. Soc. chim. France*, 1929, **45**, 308.

TABLE 1.  
Kerr effects, dielectric constants, etc., of solutions in benzene at 25°.

<i>Tropine</i>							
$10^5 w_2$ .....	396	676	711	1029	1067	1284	1410
$\epsilon^{25}$ .....	2.2799	2.2845	2.2867	2.2905	2.2939	2.2971	—
$d_4^{25}$ .....	0.87454	—	—	0.87539	0.87585	0.87601	0.87625
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 1.89$ ; $\Sigma \Delta d / \Sigma w_2 = 0.176$							
<i>Tropinone</i>							
$10^5 w_2$ .....	169	181	287	393	484	602	641
$\epsilon^{25}$ .....	2.2843	—	—	2.2988	—	—	2.3175
$d_4^{25}$ .....	—	—	—	0.87433	0.87448	—	0.87464
$10^7 \Delta B$ .....	—	0.007	0.011	—	—	0.023	—
$10^5 w_2$ .....	704	821	1024	1445	1759	2163	2314
$\epsilon^{25}$ .....	—	—	2.3429	—	2.3951	—	2.4326
$d_4^{25}$ .....	—	—	0.87538	0.87583	0.87643	0.87723	0.87738
$10^7 \Delta B$ .....	0.025	0.029	—	0.058	—	—	—
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 6.92$ ; $\Sigma \Delta d / \Sigma w_2 = 0.151$ ; $10^7 \Sigma \Delta B / \Sigma w_2 = 3.77$							
<i>3-Chlorotropane</i>							
$10^5 w_2$ .....	342	350	466	658	670	826	—
$\epsilon^{25}$ .....	2.2879	2.2890	—	—	2.3033	—	—
$d_4^{25}$ .....	0.87430	0.87435	0.87464	0.87485	0.87477	0.87512	—
$10^7 \Delta B$ .....	0.018	0.021	0.025	—	0.042	0.051	—
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 4.60$ ; $\Sigma \Delta d / \Sigma w_2 = 0.162$ ; $10^7 \Sigma \Delta B / \Sigma w_2 = 5.87$							
<i>3-Bromotropane</i>							
$10^5 w_2$ .....	401	453	531	611	698	1716	—
$\epsilon^{25}$ .....	2.2896	2.2926	2.2950	2.2975	—	—	—
$d_4^{25}$ .....	0.87498	0.87509	0.87524	0.87570	0.87606	0.87897	—
$10^7 \Delta B$ .....	0.023	—	0.031	—	0.038	0.106	—
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 4.24$ ; $\Sigma \Delta d / \Sigma w_2 = 0.303$ ; $10^7 \Sigma \Delta B / \Sigma w_2 = 5.92$							

TABLE 2.  
Calculation of results.

	$\alpha \epsilon_1$	$\beta$	$\gamma$	$\delta$	$\infty P_T$ (c.c.)	$R_D$ (c.c.)	$\mu^*$ (D)	$10^{13} \infty (mK_s)$
Tropine .....	1.89	0.202	0.000	0	88.5	37.7	1.5 <sub>2</sub>	—1
Tropinone .....	6.92	0.173	0.000	9.2	220.4	38.6	2.9 <sub>8</sub>	71
3-Chlorotropane...	4.60	0.185	0.000	14.3	182.6	43.6	2.5 <sub>3</sub>	157
3-Bromotropane...	4.24	0.347	0.000	14.4	208.4	44.7	2.8 <sub>1</sub>	202

\* Calc. for distortion polarisations of 1.05 $R_D$  (c.c.).

within the limits of experimental accuracy, with the former. Components corresponding to the moments of 1-methylpiperidine<sup>20</sup> (0.92 D) and methyl alcohol<sup>21</sup> (1.77 D), if interacting at 119°, would yield a resultant of this magnitude, but through our ignorance of both the rotational position of the C—O—H triangle and the direction of action of its moment the fact can make no useful contribution to the question of the conformation of tropine.

## DISCUSSION

*General Approach.*—Standard computational procedures exist<sup>16(c),22</sup> for calculation *a priori* of the molar Kerr constant and resultant dipole moment of a molecular structure having specifiable geometry. Selection among rival models may then be made by reference to the magnitudes of  $mK$  and  $\mu_{res}$  found by experiment. Initial data required are the longitudinal, transverse, and "vertical" polarisabilities ( $b_L$ ,  $b_T$ , and  $b_V$ ) of the bonds involved. In the present work the following are taken:

Bond	C—H	C—C	C—Cl	C—Br	C—N	C=O
$10^{25} b_L$ .....	0.064	0.099	0.382	0.530	0.057	0.230 <sub>5</sub>
$10^{25} b_T$ .....	0.064	0.027	0.185	0.270	0.069	0.140 <sub>5</sub>
$10^{25} b_V$ .....	0.064	0.027	0.185	0.270	0.069	0.046
Ref. ....	16(a)	16(a)	16(d)	16(d)	20	23

<sup>20</sup> Aroney and Le Fèvre, *J.*, 1958, 3002.

<sup>21</sup> Le Fèvre and Williams, *J.*, 1960, 108.

<sup>22</sup> Eckert and Le Fèvre, *J.*, 1962, 1081.

For each bond the three polarisabilities are related to Cartesian axes ( $X$ ,  $Y$ , and  $Z$ ), arbitrarily set up within the molecular framework, by nine direction cosines from which the polarisability of every bond along the  $X$ ,  $Y$ , and  $Z$  directions may be determined and totalled for the whole molecule. The estimate, referred to  $XYZ$ , which results is conveniently summarised by a symmetric matrix  $Q$  which, by an appropriate orthogonal transformation, affords the diagonal matrix,  $\text{diag. } (b_1 b_2 b_3)$  representing induced moments with respect to the principal axes (1,2,3). The principal semi-axes of the molecular polarisability ellipsoid and their locations within  $XYZ$  are therefore given by the eigenvalues and three orthonormal unit eigen-vectors of the matrix  $Q$ .

The direction of action of the resultant molecular dipole moment is deduced by vector addition of component bond moments; as required here these are:

Bond	(tert)N-CH <sub>3</sub>	C=O	C-Cl	C-Br
$\mu$ .....	0.92	3.12	2.18	2.26
Source .....	1-Methylpiperidine	Cycloheptanone	Cyclohexyl chloride	Cyclohexyl bromide
Ref. ....	20	23	16(d)	16(d)

For want of better information all inter-bond angles have been taken as tetrahedral. The axes  $X$ ,  $Y$ , and  $Z$  are located with  $X$  and  $Y$  in the plane  $C_{(1)}C_{(2)}C_{(4)}C_{(5)}$ ,  $X$  being parallel to the link  $C_{(1)}-C_{(2)}$ .

*Conformation of Tropinone.*—Calculations for the four models (III)—(VI) produce polarisability semi-axes,  $b_1$ ,  $b_2$ , and  $b_3$ , together with the corresponding resolutes,  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$ , of the observed dipole moment of tropinone, as in Table 3, from which, *via* the

TABLE 3.

Polarisability semi-axes, dipole moment components, etc., for tropinone.

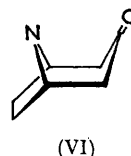
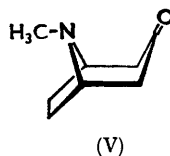
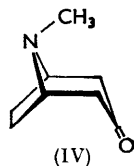
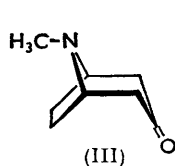
Principal polarisabilities *	Direction cosines with †			Dipole moment components ‡	Principal polarisabilities *	Direction cosines with †			Dipole moment components ‡
	X	Y	Z			X	Y	Z	
	(III)					(V)			
1.584	-0.5942	0	0.8043	-2.859	1.673	0.6613	0	0.7501	+2.918
1.537	0	1	0	0	1.537	0	1	0	0
1.451	0.8043	0	0.5942	+0.766	1.361	0.7501	0	-0.6613	-0.498 <sub>7</sub>
	(IV)				(VI)				
1.585	-0.6593	0	0.7519	-2.741	1.669	0.6860	0	0.7276	+2.699
1.537	0	1	0	0	1.537	0	1	0	0
1.449	0.7519	0	0.6593	+1.117	1.366	0.7276	0	-0.6860	-1.216

\* Listed in descending order as  $b_1$ ,  $b_2$ , and  $b_3$  in units of  $10^{-23}$  c.c. † See text for location in molecular framework. ‡ Listed in descending order as  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$ , in D.

TABLE 4.

Calculated and observed molar Kerr constants and dipole moments for tropinone.

Conformation	$10^{12} mK$ , calc.	$\mu$ (D), calc.	$10^{12} mK$ , obs.	$\mu$ (D), obs.
(III)	+75	2.7	+71	2.9 <sub>6</sub>
(IV)	+62	2.7		
(V)	+207	4.0		
(VI)	+140	2.7		



<sup>23</sup> Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

usual equations,<sup>16</sup> the molar Kerr constants for (III)—(VI) should be as in Table 4. In the 3rd column of Table 4 we also show the dipole moments forecast for (III)—(VI) by vector addition of the components (0.92 D and 3.12 D) quoted above.

Comparisons with the values from experiment show form (V) to be incompatible with both the observed moment and molar Kerr constant, and (VI) to be incompatible with the second of these properties. Either of the forms (III) and (IV) is admissible; therefore tropinone contains a chair-type piperidone ring, and consequently (cf. refs. 8—10) so also do tropine and  $\psi$ -tropine.

*Conformation of the N-Me Link.*—The disposition of the methyl group in tropinone unfortunately is not conclusively demonstrated by the foregoing results. Our calculations are therefore extended to include 3-chloro- and 3-bromo-tropane, two derivatives formed from tropine by interaction with the appropriate hot aqueous hydrogen halide. The literature contains no direct physical proof of their space formulæ. However, replacement of alcoholic hydroxyl groups by halogen acids is said to occur predominantly with inversion (cf. Ingold, ref. 24, p. 393). In addition, Archer *et al.*<sup>25</sup> have obtained a mixture of nitriles from chlorotropane, comparable with that which results from a similar treatment of  $\psi$ -tropine toluene-*p*-sulphonate. Since inversion in the preparation of the sulphonate is unlikely, they conclude that inversion has occurred in the formation of chlorotropane from tropine. Accepting this, and having in mind the easy boat-chair transformation of  $\psi$ -tropine, we have made calculations for the eight conformations shown as (VII)—(X), where X = Cl or Br. These are summarised in Tables 5 and 6; Table 6 also includes the resultant moments predicted for the respective conformations, when components of 0.92, 2.18, or 2.26 D are taken for  $\mu_{N-CH_3}$ ,  $\mu_{C-Cl}$ , or  $\mu_{C-Br}$  (see above).

TABLE 5.  
Polarisability semi-axes, dipole moment components, etc., for  
3-chloro- and 3-bromo-tropane.\*

Principal polarisa- bilities	Direction cosines with			Dipole moment com- ponents	Principal polarisa- bilities	Direction cosines with			Dipole moment com- ponents
	X	Y	Z			X	Y	Z	
	(VII) X = Cl					(IX) X = Cl			
1.839	0.9945	0	0.1043	+2.511 <sub>4</sub>	1.792	0.0464	0	0.9989	+2.534 <sub>0</sub>
1.646	0	1	0	0	1.661	0.9989	0	-0.0464	-0.4852
1.614	-0.1043	0	0.9945	+0.5911	1.646	0	1	0	0
	(VII) X = Br					(IX) X = Br			
1.986	0.9967	0	0.0816	+2.726 <sub>7</sub>	1.934	-0.0755	0	0.9971	+2.802 <sub>7</sub>
1.731	0	1	0	0	1.752	0.9971	0	0.0755	-0.202 <sub>6</sub>
1.700	-0.0816	0	0.9967	+0.679 <sub>2</sub>	1.731	0	1	0	0
	(VIII) X = Cl					(X) X = Cl			
1.848	0.9968	0	0.0802	+2.571 <sub>7</sub>	1.781	0.0212	0	0.9998	+1.978 <sub>0</sub>
1.646	0	1	0	0	1.672	0.9998	0	-0.0212	-1.655 <sub>4</sub>
1.605	-0.0802	0	0.9968	-0.2069	1.646	0	1	0	0
	(VIII) X = Br					(X) X = Br			
1.996	0.9980	0	0.0638	+2.804 <sub>3</sub>	1.924	-0.1082	0	0.9941	+2.385 <sub>1</sub>
1.731	0	1	0	0	1.762	0.9941	0	0.1082	-1.485 <sub>3</sub>
1.690	-0.0638	0	0.9980	-0.179 <sub>3</sub>	1.731	0	1	0	0

\* Footnotes from Table 3 apply here.

It is seen that the observed  $mK$  of the chloro-derivative is between those calculated for forms (VII) and (VIII), and that of the bromo-analogue is nearest to the  $mK$  expected for form (VII). Chair rather than boat forms are thus indicated. Further discrimination

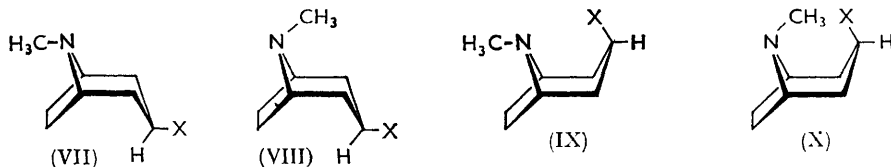
<sup>24</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953.

<sup>25</sup> Archer, Lewis, and Zenitz, *J. Amer. Chem. Soc.*, 1958, **80**, 958.

TABLE 6.

Calculated and observed molar Kerr constants and dipole moments for  
3-chloro- and 3-bromo-tropine.

Solute	Conformation	$10^{12} K$ , calc.	$\mu$ (D), calc.	$10^{12} K$ , obs.	$\mu$ (D), obs.
3-Chlorotropine .....	VII	143	2.6	} 157	} 2.5 <sub>3</sub>
	VIII	164	1.3		
	IX	98	3.0		
	X	41	2.6		
3-Bromotropine ...	VII	218	2.7	} 202	} 2.8 <sub>1</sub>
	VIII	251	1.3		
	IX	168	3.0		
	X	97	2.7		



between types (VII) and (VIII), by comparing the  $\mu$ 's calc. and found, leaves (VII) as the most appropriate conformation in each case.

It must be emphasised that this assignment depends crucially on the stereochemistry of the  $\text{ROH} \rightarrow \text{RX}$  reaction, *i.e.*, on the relation of chloro- and bromo-tropine to  $\psi$ -tropine. If the C-X links were attached axially to chair piperidine skeletons, calculations parallel to those of Tables 5 and 6 would appear as follows:

Solute	Conformation of N-CH <sub>3</sub>	$10^{12} K$ , calc.	$\mu$ (D), calc.
3-Chlorotropine .....	{ Equatorial	147	1.3
	{ Axial	132	2.6
3-Bromotropine .....	{ Equatorial	230	1.3
	{ Axial	206	2.7

and our measurements then would favour axial dispositions for both the C-X and the N-CH<sub>3</sub> bonds. Ingold's review,<sup>24</sup> however, strongly suggests that in the reaction in question inversion is general except when a "configuration-retaining" substituent is affecting the intermediate hydrogen-bond complex presumed to be first formed. Cowdrey, Hughes, Ingold, Masterman, and Scott<sup>26</sup> explicitly cite the presence of electron-releasing groups as powerful configuration-preserving factors. In tropine neither the ethylene bridge from C<sub>(1)</sub> to C<sub>(5)</sub>, nor a cationic nitrogen atom—inevitable in a strongly acid medium—has such electron-releasing qualities; the tropine  $\rightarrow$  halogenotropine reactions should accordingly be expected to occur with inversion, and of the two possible conclusions regarding form (VII) that given first is therefore to be preferred.

Although not completely parallel to the tropine situation, Shoppee's demonstration<sup>27</sup> of inversion during the change of cholestan-3-ol into 3-chlorocholestane and of retention of configuration during the same reaction with cholesterol (when the electron releasing 5,6-double bond is present) affords indirect support for the choice just made.

Acknowledgment is made to the C.S.I.R.O. for the award of a Senoir Research Studentship to J. M. E.

UNIVERSITY OF SYDNEY, SYDNEY, N.S.W., AUSTRALIA.

[Received, December 27th, 1961.]

<sup>26</sup> Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1252.

<sup>27</sup> Shoppee, *J.*, 1946, 1138, 1147.