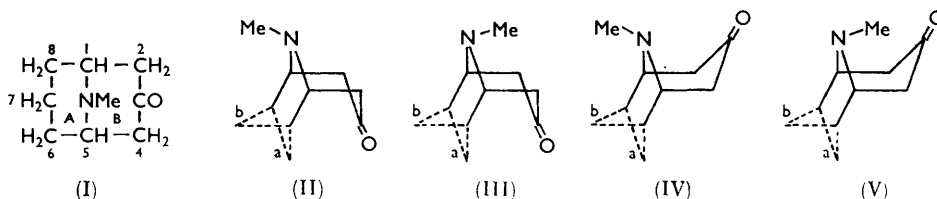


### 61. Molecular Polarisability: the Conformation of $\psi$ -Pelletierine as Solute in Benzene.

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The dipole moment ( $2.7_{\text{D}}$ ) and molar Kerr constant ( $81 \times 10^{-12}$ ) of  $\psi$ -pelletierine in benzene, together with a consideration of steric compressions in scale models, suggest that the solute molecules mostly have ring B in the chair conformation, and that at least 50% of them have ring A likewise.

THE pomegranate alkaloid,  $\psi$ -pelletierine (I), poses stereochemical problems analogous to those of the related tropinone,<sup>1</sup> although ring A is here 6-membered and can also exist in chair or boat form. Eight conformations are therefore possible in which the piperidine rings A and B are in the chair or boat form and the *N*-methyl group has one of its two possible positions (II—V).



From dipole moment and infrared studies, Leonard *et al.*<sup>2</sup> eliminated conformations (IVa and b), and they noted that molecular models indicated significant steric compression in conformations (Va and b), and generally less compression in boat-chair than in chair-chair combinations of rings A and B. Their conclusion, accordingly, was that conformations resembling (IIb) or (IIIb) are favoured.

The subject appeared to be one to which the Kerr effect could be usefully applied; appropriate measurements of  $\psi$ -pelletierine as a solute in benzene are now reported.

#### EXPERIMENTAL

*Solute, Solvent, Methods, etc.*— $\psi$ -Pelletierine, prepared by the directions of Cope, Dryden, and Howell,<sup>3</sup> had m. p.  $62-64^{\circ}$ . Freshly distilled, sodium-dried benzene was used as solvent. The dielectric constants  $\epsilon$ , densities  $d$ , and Kerr constants  $B$  of solutions containing weight fractions  $w$  of solute are listed in Table 1. Experimental methods have been those described

TABLE I.

Dielectric constants, densities, and incremental Kerr constants \* for solutions of  $\psi$ -pelletierine in benzene at  $25^{\circ}$ .

$10^5 w_2$ ...	578	727	874	939	1332	1349	1547	1579	1584	2427
$\epsilon$ .....	—	2.3128	—	2.3233	—	2.3465	2.3569	—	—	2.4051
$d$ .....	—	0.87502	0.87539	0.87548	—	0.87591	0.87642	—	—	0.87774
$10^7 \Delta B$	0.022	0.025	0.032	0.031	0.049	—	—	0.057	0.057	—

\* Over the concentrations used, differences  $\Delta n$  between the Me refractive indices of solutions and solvent were beneath detection.

in ref. 4, wherein symbols are also defined; ref. 5 summarises the equations used on the quantities actually observed. When  $w = 0$ ,  $\epsilon = 2.2725$ ,  $d = 0.87378$ ,  $n_D = 1.4973$ , and

<sup>1</sup> Eckert and Le Fèvre, *J.*, 1962, (a) 3991, (b) 1081.

<sup>2</sup> Leonard, Morrow, and Rogers, *J. Amer. Chem. Soc.*, 1957, **79**, 5476.

<sup>3</sup> Cope, Dryden, and Howell, *Org. Synth.*, 1957, **37**, 73.

<sup>4</sup> Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; Ch. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.

<sup>5</sup> Le Fèvre and Sundaram, *J.*, 1962, 1494.

$B_D = 0.410 \times 10^{-7}$  at  $25^\circ$ . The results give:  $\Sigma\Delta\epsilon/\Sigma w_2 = 5.47$ ,  $\Sigma\Delta d/\Sigma w_2 = 0.169$ , and  $10^7\Sigma\Delta B/\Sigma w_2 = 3.60$ . With  $\alpha\epsilon_1 = 5.47$ ,  $\beta = 0.193$ ,  $\gamma = 0$ , and  $\delta = 8.8$ , we have (by the usual expressions <sup>4,6</sup>):  ${}_\infty P_2 = 199.7$  c.c.,  $R_D = 41.4$  c.c.,  $\mu = 2.7_6$  D (if  ${}_D P = 1.05 R_D$ ), and  ${}_\infty(mK_2) = 81 \times 10^{-12}$ . For comparison, we note that Leonard *et al.*<sup>2</sup> gave for (I) under present conditions,  ${}_\infty P_2 = 198.5$  c.c.,  $R_D = 43.5$  c.c., and  $\mu = 2.7_5$  D; agreement as to polarity is therefore satisfactory. The recorded moment of tropinone ( $2.9_6$  D)<sup>1a</sup> is slightly higher than that of  $\psi$ -pelletierine.

## DISCUSSION

By procedures set out in ref. 1b, and by using as a basis the bond moments and bond polarisability semi-axes given in ref. 1a, calculations have been made of the principal molecular polarisability semi-axes,  $b_1$ ,  $b_2$ , and  $b_3$ , to be expected for each of the models (II)—(V), and therefrom the corresponding molar Kerr constants,  ${}_m K_{\text{calc.}}$ . For want of precise information, inter-bond angles have been taken as tetrahedral throughout. Results are shown as Tables 2 and 3. The locations of  $b_1$ ,  $b_2$ , and  $b_3$  are defined by reference to mutually perpendicular axes ( $OX$ ,  $OY$ ,  $OZ$ ) placed with  $OX$  and  $OY$  in the 1,2,4,5-plane and  $OZ$  parallel to the 1,2-link.

TABLE 2.

Polarisability semi-axes, dipole-moment components, etc., for  $\psi$ -pelletierine.

Conformn.	Principal polarisability semi-axes *	Direction cosines with			Dipole-moment components *
		X	Y	Z	
IIa	1.795	-0.5516	0	0.8341	-2.63
	1.701	0	1	0	0
	1.614	0.8341	0	0.5516	0.85
IIIa	1.795	-0.6027	0	0.7980	-2.63
	1.701	0	1	0	0
	1.614	0.7980	0	0.6027	-0.85
IVa	1.844	0.6112	0	0.7914	2.74
	1.701	0	1	0	0
	1.564	0.7914	0	-0.6112	-0.29
Va	1.838	0.6386	0	0.7696	2.58
	1.701	0	1	0	0
	1.570	0.7696	0	-0.6386	-0.97
IIb	1.753	-0.6525	0	0.7578	-2.71
	1.701	0	1	0	0
	1.655	0.7578	0	0.6525	0.51
IIIb	1.757	0.7297	0	-0.6837	2.44
	1.701	0	1	0	0
	1.652	0.6837	0	0.7297	-1.29
IVb	1.875	0.6919	0	0.7220	2.70
	1.701	0	1	0	0
	1.534	0.7220	0	-0.6919	-0.58
Vb	1.871	0.7143	0	0.6999	2.47
	1.701	0	1	0	0
	1.538	-0.6999	0	0.7143	1.23

\* Listed in descending order as  $b_1$ ,  $b_2$ , and  $b_3$  (in  $10^{-23}$  c.c.) and  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$  (in D.), respectively.

TABLE 3.

Calculated and observed molar Kerr constants and dipole moments for  $\psi$ -pelletierine.

Conformn.	$10^{12} {}_m K_{\text{calc.}}$	$\mu^*$ (D) calc.	$10^{12} {}_m K_{\text{obs.}}$	$\mu$ (D) obs.	Conformn.	$10^{12} {}_m K_{\text{calc.}}$	$\mu^*$ (D) calc.
IIa	95	2.7			IIb	59	2.7
IIIa	95	2.7			IIIb	39	2.7
IVa	177	4.0			IVb	202	4.0
Va	131	2.7	81	$2.7_6$	Vb	132	2.7

It is seen that the predicted moments and molar Kerr constants for models (IVa and b) are incompatible with those observed; for models (Va and b) the moments are acceptable

but the molar Kerr constants forecast are too high. The  ${}_mK$  found could be reconciled with a mixture of (Va or b) and (IIb or IIIb) but an appreciable content of (Va or b) seems unlikely in view of the steric compression between the oxygen atom and the *N*-methyl group already noted<sup>2</sup> in models of this conformation.

If considerations are restricted to models (II) and (III), a comparison of observed and calculated  ${}_mK$ 's fails to confirm the suggestion of Leonard *et al.*<sup>2</sup> that species having ring A as a boat predominate [ ${}_mK_{\text{obs}}$  is 25—30% and 50% in excess of  ${}_mK_{\text{calc}}$  for models (IIb) and (IIIb), respectively]; rather it appears that solute forms are present (as a mixture or equilibrium) with at least 50% of the A rings as chairs (*i.e.*, as IIa or IIIa). Unfortunately the calculations do not differentiate between alternative configurations around the nitrogen atom.

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