c	$\Delta\varepsilon$	$\varepsilon^{25}_{\text{Dioxane}}$	P_M	μ
0.00415	0.0247 ± 0.0005	2.2103	1000 ± 20	7.0 D
0.00208	0.0130 ± 0.0005		1058 ± 40	
0.00104	0.0065 ± 0.0005		1058 ± 80	

The accuracy with which P_M can be determined in these very dilute solutions is too small to allow any reliable extrapolation to zero concentration. The solutions measured are, however, so dilute that P_M has probably already reached its maximum value. The true dipole moment can therefore not be much larger than 7.0 D, the value calculated from P_M of the most concentrated solution.

As expected the dipole moment of pyocyanine is rather large, showing that a highly dipolar structure plays an important rôle in determining the actual state of the molecule. Although there are other possible dipolar resonance structures, the only one of importance is probably that pictured as II. On the basis of the known bond lenghts and valency angles, a dipole moment of approximately 24 D can be calculated for this structure. Since the dipole moment of the single bond C—N is only small, the dipole moment of the ortho quinoid structure I should be almost exclusively determined by the moments of the bonds $>C = O$ and $>C = N-$. The first is about 2.5 D and the second is 1.6 D[9], so that the dipole moment of structure I may be taken as $\sqrt{2.6^2 + 1.6^2 + 2.6 \times 1.6}$ = 3.6 D. If is assumed that the resulting dipole moment can be calculated from formula [10]:

$$\mu = (1-x_{II})\mu_I + x_{II}\mu_{II}$$

where μ is the dipole moment found and μ_I and μ_{II} are the moments calculated for structure I and II, the fractional contribution of the polar structure should be $x_{II} = 0.17$.

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The Dipole Moment of Sempervirine

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According to Prelog[1] sempervirine, the brown alkaloid of *Gelsemium sempervirens*, has the structure I. Woodward and Witkop[2], however, have presented evidence in favour of describing the molecule in terms of a resonance hybrid of structures II and III. This proposal accounts very well for the chemical and physical properties of sempervirine, but it remains to be shown that sempervirine has the high dipole moment required, if structure III makes a significant contribution to the state of the molecule.

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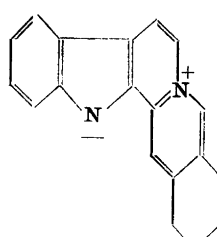Kushner, L. M., and Smyth, C. P. *Ibid.* **71** (1949) 1403.
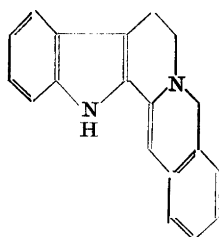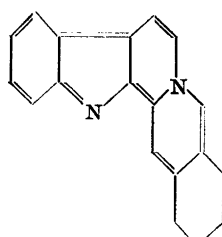
I   II   III

Sempervirine is very slightly soluble in most solvents. The dielectric constant of almost saturated solutions in dioxane and benzene (which have a very intense golden colour), however, differ measurable from those of the pure solvents. On the basis of these measurements the dipole moment of sempervirine has been estimated to be 7—8 D, a very high value, indicating that the structure III is of definite importance for the actual state of the molecule. The reaction of sempervirine with alkyl halides (Woodward and Witkop, *l. c.*) is analogous to the reaction of unambiguous dipolar ions with alkyl halides (*cf.* Jensen and Friediger [3]).

The dipole moment was determined as described in a previous publication [4].

Table 1. Dipole moment of sempervirine
($C_{19}H_{16}N_2 \cdot H_2O$) in dioxane at 22° C.

Molar conc.	ε	$\varepsilon_{Dioxane}$	P_M	μ
0.001711 (4.962 mg/10 ml)	2.2250	2.2095	1532	8.5 D
0.000851 (2.468 mg/10 ml)	2.2170	2.2095	1504	

Table 2. Dipole moment of sempervirine in benzene at 22° C.

Molar conc.	ε	$\varepsilon_{Benzene}$	P_M	μ
0.00076 (2.200 mg/10 ml)	2.2840	2.2785	1186	7.5 D

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