DIPOLE MOMENTS OF CAMPHOR COMPOUNDS*—PART I

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1. Introduction

From a consideration of the Bredt graphic formula for camphor one might expect that apart from the optical isomers, there are also *cis-trans* isomers due to the puckered six-membered ring. The X-ray investigation of *d*-α, Br, Cl and CN camphors carried out by Wiebenga and Krom (1946) points out to the " boat shape " of the six-membered ring of camphor. Measurements of the dipole moments of some camphor compounds were carried out in order to supplement the study of the structure of the camphor ring. In this paper the dipole moments of camphorquinone, camphor oxime and *iso*-nitroso camphor have been reported and discussed in the light of the X-ray structure of camphor.

2. Experimental

Materials.—Benzene ' Analar ' was repeatedly shaken with concentrated sulphuric acid, washed with water, dried over calcium chloride and then over sodium wire. After fractionation, the middle portion was frozen out and finally stored over sodium wire which retained its metallic lustre. B.Pt. = 80·5° (759 mm.); $d_4^{35} = 0{\cdot}86278$; $n_D^{35} = 1{\cdot}4910$.

d-Camphorquinone (B.D.H.) and *d*-camphor oxime (B.D.H.) were crystallized several times from absolute ethyl alcohol [M.Pt. (uncorr.) 199° and 118° respectively]. *iso*-Nitroso camphor (anti) was prepared according to Forster's (1904) method. M.Pt. (uncorr.) 152·5°.

Apparatus.—For the measurement of dielectric constants a heterodyne beat apparatus similar to the one described by Hudson and Hobbs (1942) was used with the following modifications. The 1000 kc./sec. oscillator employed in the present apparatus was operated with a type 6V6 tube and the plate supply for the tubes was obtained from an electronic

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voltage regulator using type 6J7 and type 2A3 tubes. A valve maintained tuning fork was employed for reference and the whole apparatus electrically shielded and maintained at a uniform temperature. The dielectric cell used was of the Sayce-Briscoe type.

3. RESULTS

The mathematical extrapolation method of Hedestrand (1929) was employed for the computation of dipole moments from the dielectric constant and density data of dilute solutions. The contribution due to atom polarisation was taken to be 5% of the molar refraction (MR_D). Tables I to III summarize the results obtained. All measurements were made at a temperature of 35° C. $\pm$ 0·02.

TABLE I

d-Camphorquinone in Benzene

No.	Mole fraction $f_1 \times 10^6$	Dielectric constant ϵ	Density d	$\alpha\epsilon_2$	β
1	0	2·2535	0·86278	..	..
2	3,065	2·3433	0·86376	29·30	0·375
3	4,513	2·3823	0·86431	28·54	0·398
4	5,933	2·4363	0·86488	30·82	0·415
5	8,428	2·5172	0·86578	31·29	0·417
6	10,882	2·5754	0·86674	29·58	0·427

Total polarisation $_TP_\infty$ = 505·5 c.c. 1·05 MR_D = 49·6 c.c.
Orientation polarisation $_0P$ = 455·9 c.c. μ = 4·78 D

TABLE II

d-Camphor Oxime in Benzene

No.	$f_1 \times 10^6$	ϵ	d	$\alpha\epsilon_2$	β
1	0	2·2535	0·86278	..	..
2	8,502	2·2698	0·86541	1·917	0·309
3	10,698	2·2712	0·86600	1·655	0·301
4	14,453	2·2801	0·86715	1·841	0·302
5	16,665	2·2844	0·86780	1·854	0·301
6	23,208	2·2928	0·86963	1·693	0·295

$_TP_\infty$ = 76·71 c.c. 1·05 MR_D = 49·74 c.c. $_0P$ = 26·97 c.c. μ = 1·16 D.

TABLE III

iso-*Nitroso Camphor in Benzene*

No.	$f_1 \times 10^6$	ϵ	d	$\alpha\epsilon_2$	β
1	0	2·2535	0·86278	..	..
2	8,772	2·3860	0·86670	15·105	0·518
3	10,298	2·4104	0·86768	15·236	0·552
4	13,378	2·4601	0·86906	15·443	0·544
5	16,202	2·5001	0·87022	15·220	0·532
6	18,401	2·5371	0·87100	15·412	0·518

$_TP_\infty$ = 280·20 c.c. 1·05 MR_D = 49·52 c.c. $_0P$ = 230·68 c.c. μ = 3·40 D.

4. DISCUSSION

Representing the molecule of camphor with the numbering of carbon atoms as shown in Fig. 1, the atoms 1, 2, 3, 4 and 10 are shown by X-ray analysis to lie in a plane (I) while atoms 6 and 5 with the bonds 1–6, 6–5 and 5–4 lie in another plane (II). Similarly atom 7 and bonds 1–7 and 4–7 constitute the other plane (III). Consequently one may speak of planes II and III as forming a " fork " from the plane I.

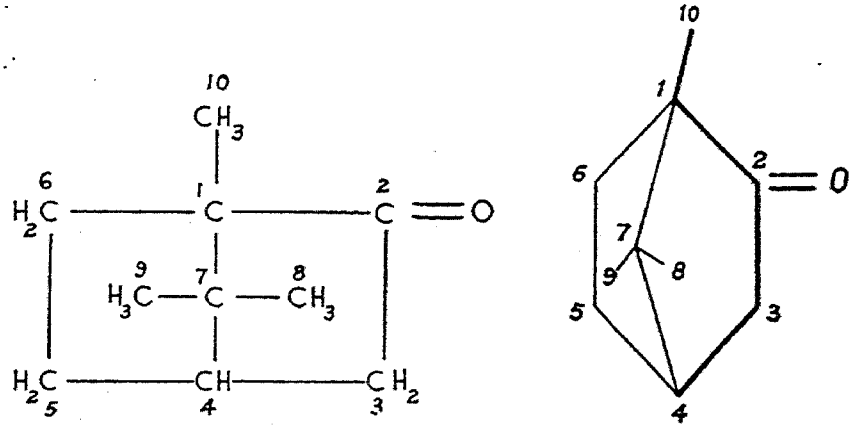

FIG. 1

The total moment of a molecule may be calculated by vectorial addition of the various bond moments. In the case of camphor there is only one strong primary dipole (C = O) as the C—H bond moments may be taken as mutually cancelling each other. This primary dipole will however induce moments of finite magnitude in the neighbouring atoms and groups and account must be taken of such induced moments in calculating the total moment of the molecule. In the present paper the moment contribution

from the planar part (I) of the molecules has been calculated by the method of Groves and Sugden (1937) and the value so obtained compared with the total moment to obtain the moment contribution from the two planes II and III forming the "fork". Such calculations give a good idea of the general disposition of dipoles with regard to the "fork" in these molecules. Table IV gives the result of calculations carried out for the planar part (I) of camphor according to the method of Groves and Sugden, the notations used here being the same as those used by these authors.

TABLE IV

Induced Moments in Plane I of Camphor

(in terms of $\mu C=O$)

No. of atom or group (see Fig. 1 for notations used)	μ_{ix}	μ_{iy}
1	0·0534	0·1160
3	0·1011	0·2192
4	0·0464	0·0214
10	−0·0750	0·0933

Taking a value of 2·3 D for $\mu C=O$, the moment contribution from the planar part (I) of camphor is found to be 2·64 D from the appropriate structural diagram while the observed moment of the molecule is 3·0 D (*Tables of Dipole Moments*, 1934).

The moment contribution from the "fork" is therefore 0·36 D. The results of similar calculations carried out for camphorquinone are given in Table V, where the subscripts 1 and 2 refer to the two C = O dipoles.

TABLE V

Induced Moments in Plane I of Camphorquinone

(in terms of $\mu C=O$)

No. of atom or group (see Fig. 1 for notations used)	μ_{ix1}	μ_{ix2}	μ_{iy1}	μ_{iy2}
1	0·0534	0·3192	0·1160	0·3377
4	0·0460	0·0772	0·0210	0·1674
10	−0·0750	0·3441	0·0933	0·4724

The moment contribution from the planar part (I) of this molecule obtained from the appropriate structural diagram is 3·99 D. The observed moment of the molecule being 4·78 D, the contribution due to the "fork" in this molecule is 0·79 D as compared to 0·36 D in the case of camphor. This result suggests a symmetric disposition of the two C = O dipoles with regard to the "fork" in camphorquinone.

Camphor oxime is an interesting case in that chemical resolution of this compound into its two possible isomers has not yet been effected. The dipole moments of the two structures were calculated and the difference was found to be negligibly small. Consequently, the experimentally obtained value will be taken as such in the present discussion. In a preliminary calculation of the moment contribution due to the planar part (I) of this molecule a value of 1·68 D was obtained on the assumption of free rotation of the OH group in = N—OH. The observed moment of the molecule should be greater than this value since the moment contribution from the "fork" has not been added. The moment contribution from the planar part of this molecule in the case of the two extreme structures (A) and (B) represented in Fig. 2 were calculated from the appropriate structural diagrams and found to be 2·67 D and 0·77 D respectively.

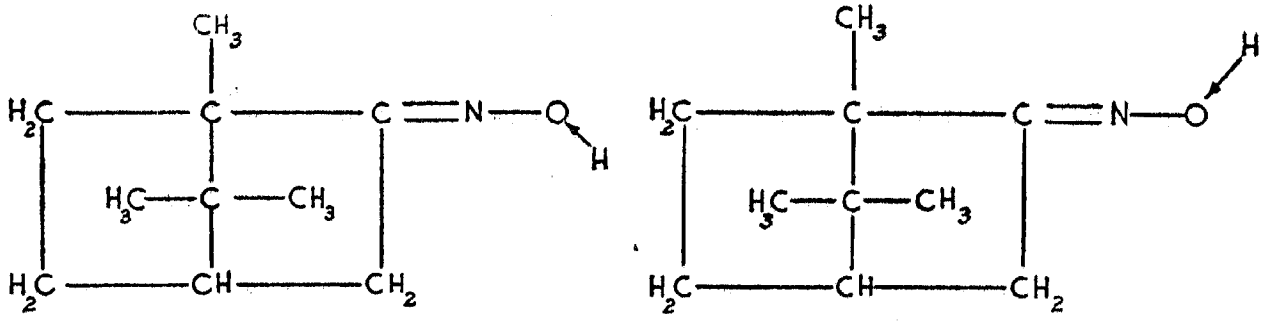

FIG. 2

In accordance with our earlier deduction, the moment contribution due to the "fork" in these structures will be approximately directly proportional to the primary dipole vector and thus the experimental value of 1·16 D seems to favour structure (B) with probably hindered rotation of the OH group. Calculations similar to those given above were carried out in the case of *iso*-nitroso camphor (anti) and a value of 3·14 D was obtained for the moment contribution from the planar part of this molecule on the assumption of free rotation of the OH group. This is in good agreement with the experimental value of 3·4 D obtained for this molecule.

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5. SUMMARY

The dipole moments of camphorquinone, camphor-oxime and *iso*-nitroso camphor have been determined and discussed in the light of the values calculated by the vector addition of bond moments.

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