DIPOLE MOMENTS OF CAMPHOR COMPOUNDS*

Part II. The Dipole Moments of dl-Borneol, Camphoric Acid and 3-Bromo-Camphorenic Acid

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THE stereochemical characteristics of the camphor group present several interesting features and the present studies have been initiated as an approach to some aspects of the problem. One of us (P. T. N.) has reported the results with some camphor derivatives while the present communication deals with a further batch.

It has to be remarked here that, while extensive measurements of the dipole moments of the esters of dicarboxylic acids are available, the corresponding acids themselves do not appear to have received the same attention. The comparative insolubility of these compounds in nonpolar solvents has been the obstacle. However, camphoric acid, though insoluble in benzene, is sufficiently soluble in dioxan to permit of direct measurements on the free acid. Wilson and Wenzke (15) working with monocarboxylic acids report the absence of any association in this solvent but our experimental observations do not support this view. The results of observations on 3-bromocamphorenic acid in benzene provide a means for comparison with monocarboxylic acids.

LeFevre and Maramba (9) have recently reported on some peculiarities in the polarisations of antipodes in the terpene series and our results with borneol confirm these observations:

EXPERIMENTAL

Materials.—Benzene was purified as indicated in Part I (11); 1:4-Dioxan was purified by the method of Eigenberger (4). B.p. 101° C. (755 mm.) d_4^{35}: 1·01690 n_D^{35}: 1·4150: 2·1778;

d-Camphoric acid (Kahlbaum) was repeatedly purified by recrystallisation from absolute alcohol, m.p. (uncorr.) 187° C.

3-Bromocamphorenic acid was prepared by the method of Shive and co-workers (13). The final product after recrystallisation from benzene had a m.p. 181° C. (uncorr.).

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dl-Borneol (B.D.H.) was recrystallised several times from absolute alcohol and then several times from pure benzene.

The final product had a m.p. of 212° C. (sealed tube). All measurements have been carried out in the same apparatus as described in Part I (*loc. cit.*)

RESULTS

The extrapolation method of Hedestrand was used in the computation of dipole moments from the data on dilute solutions. The atom Polarisation was assumed to be 5% of the molar refraction. All measurements have been made at 35° C. The results are presented in Tables I–III.

TABLE I

dl-Borneol in Benzene Solution

Mole fraction of solute $f_1 \times 10^6$	ϵ	d	at_2	β
0	2·2535	0·86278	..	..
0·8070	2·2905	0·86430	4·584	0·218
1·1251	2·3048	0·86490	4·560	0·218
1·2370	2·3098	0·86515	4·552	0·222
1·7491	2·3331	0·86607	4·552	0·218
1·9760	2·3429	0·86651	4·524	0·219

$_TP_\infty = 116\cdot5$ c.c. $1\cdot05\ _RM_D = 44\cdot1$ c.c. $_oP = 72\cdot4$ c.c.
$\mu: 1\cdot85$ D

TABLE II

3 Br-Camphorenic Acid in Benzene Solution

$f_1 \times 10^6$	ϵ	d	at_2	β
0	2·2535	0·86278	..	..
1·386	2·2584	0·86431	3·535	1·280
4·405	2·2674	0·86725	3·148	1·176
5·204	2·2688	0·86805	2·940	1·174
7·597	2·2791	0·87016	3·370	1·126
9·251	2·2842	0·87227	3·319	1·189
10·530	2·2883	0·87350	3·305	1·180

$_TP_\infty = 103\cdot85$ c.c. $1\cdot05\ _MR_D = 54\cdot0$ c.c. $_oP = 49\cdot85$ c.c.
$\mu: 1\cdot58$ D

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TABLE III

d-Camphoric Acid in Dioxan Solution

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Mole fraction $f_1 \times 10^6$	ϵ	d	αt_2	β
0	2·1778	1·01690	..	..
10·077	2·2813	1·02030	10·271	0·332
14·050	2·3190	1·02195	10·050	0·354
16·101	2·3320	1·02221	9·577	0·324
19·197	2·3503	1·02320	8·625	0·323

$$_T P_\infty = 190 \cdot 7 \text{ c.c.} \qquad 1 \cdot 05 \, _M R_D = 48 \cdot 3 \text{ c.c.} \qquad _O P = 142 \cdot 4 \text{ c.c.}$$
$$\mu = 2 \cdot 70 \text{ D}$$

DISCUSSION

The dipole moment for *dl*-Borneol recorded here appears to be much higher than those reported by earlier workers. Donle and Wolf (3) reported 1·56 D for the *l*-variety while Higashi reported 1·65 D for the inactive form (8). Halverstadt and Kumler (6) have pointed out the possible errors in working with high dilutions but we have to presume the absence of these since both dielectric constant and density values show a strictly linear relationship with the concentration in our observations, leading to the limiting value for the pure solvent in each case. The discrepancy has then to be traced to other causes. As has been indicated in Part I as well as in the work on Pyran compounds (Anantakrishnan and Soundararajan, 1), greater accuracy can be claimed now both for the extrapolation methods used and for the experimental set-up. Another possible cause of discrepancy is the difference in the concentration range used. Higashi's work uses the molefraction range 0·0283 to 0·0822 while the present work is with the more dilute solution with the molefraction range 0·00807 to 0·01976.

Using tartrates as examples, Cotton (2) has shown that in water salts of racemic acid are different from equivalent mixtures of the two tartrates and one may expect a similar state of affairs with other optically active compounds as has been shown to be the case by LeFevre and Maramba (*loc. cit.*). In the present case one may legitimately expect that even in benzene solution we are dealing with an equilibrium

$$(+ \; -) \rightleftharpoons (+) + (-)$$
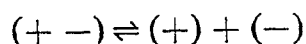
in which the position may be slightly shifted with temperature. If association between the antipodes takes place, the apparent polarisation at any

given concentration of the racemate will be different from that of the single component. Taking these into account, one can readily account for the differences noticed. Further work with the pure components and over a larger range of concentration as well as of temperature is needed before the phenomenon can be understood.

The carboxylic acids are of interest from a different angle. The cyclohexane ring in camphor is known to be multiplanar, having the " boat " form and the bridge is also not in the same plane but the position may not be the same in the products of oxidation. In 3-Bromo camphorenic acid we have to consider the interaction of moments due to the presence of a double bond, the bromine atom and the carboxylic group while in camphoric acid we have the mutual interaction of two carboxyl groups attached to 1 : 3 carbon atoms. As indicated earlier, we have the further complication in the latter case of having dioxan as the solvent.

In the present state of our knowledge of group interactions, evaluation of the dipole moment of the bromocamphorenic acid from group moments and mesomeric moments is not feasible but one may expect the value to be less than that of bromocyclohexane but more than that of cyclohexane carboxylic acid and the value observed is in this range.

From the stereochemical configuration of camphor, known from physical evidence, one may expect at least three different forms for camphoric acid but the form that is generally obtainable is one which readily forms an anhydride and can reasonably be presumed to have both carboxylic acid groups on the same side of the plane of the cyclopentane ring. This is further indicated by the large dipole moment observed. While this qualitative conclusion can be drawn, the actual value of the moment is liable to two sources of error. Solvent solute association can vitiate results and as indicated by Sutton (14) where large moments are involved the assumption that atom polarisation is small cannot be justified.

Wilson and Wenzke (*loc. cit.*) observe from the measurements on the dipole moments of monocarboxylic acids in dioxan that the values approximate to those in the gaseous phase. They consider that as a solvent containing oxygen in its structure, it is able to break up the hydrogen bonds of the acid molecules, thereby leading to the values of the monomer. It is implicit here that there is interaction between solvent and solute. Further, Haggis has clearly shown that in hydrogen bonded substances, solvent solute reaction is invariably present (5). Our results in Table III show that the value of ζa varies inversely as the concentration of the camphoric acid. This is a clear indication that there is interaction between

dioxan and the acid, besides a possible intermolecular association. The moment observed is probably that of the complex rather than the monomer and the coincidence observed by Wilson and Wenzke may be fortuitous (*cf.*, also LeFevre and Vine, 10).

The evidence from measurements of relaxation times is also not definite. Potopenko and Wheeler (12) from measurements on monocarboxylic acids in dioxan conclude that τ dioxan is uninfluenced by these solutes while Haggis (*loc. cit.*) using water as the solute draws a different conclusion. It is clear that fuller investigations on both dipole moments and relaxation times in dioxan and other solvents with mono and dicarboxylic acids as solutes is necessary. We can, however, safely consider that, taking the trend in values, dioxan solutions depart from ideal behaviour and as such the moment values cannot be the same as that in the gas phase.

SUMMARY

Dipole moment measurements on *dl*-borneol, 3-bromocamphorenic acid and camphoric acid are reported. The results with dilute solutions of *dl*-borneol indicate a possible independent existence of the antipodes in very dilute solutions besides the racemic form. The values for camphoric acid in dioxan demonstrate the presence of solvent-solute interactions in this solvent.

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