STUDIES ON THE NATURE OF THE RACEMIC MODIFICATIONS OF OPTICALLY ACTIVE COMPOUNDS IN THE SOLID STATE

Part XIII. Camphor-β-sulphonyl *o*-, *m*- and *p*-nitro phenylamides (*d*- and *dl*-), camphor-β-sulphonyl *o*-, *m*- and *p*-phenylene diamines (*d*- and *dl*-) and *o*-, *m*- and *p*-phenylene-*bis*-camphor-β-sulphonylamides (*d*- and *dl*-)

BY BAWA KARTAR SINGH, F.A.SC. AND SHIVA MOHAN VERMA

(Organic Chemistry Research Section, Banaras Hindu University, Banaras)

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IN this communication, which is in continuation of our previous work,[1] we describe the investigation of the nature of the racemic modifications of camphor-β-sulphonyl-nitro phenylamides (*o*, *m*- and *p*-), camphor β-sulphonyl-phenylene diamines (*o*-, *m*- and *p*-) and phenylene-*bis*-camphor-β-sulphonylamides (*o*-, *m*- and *p*-). Out of the three methods described previously by us,[2, 3, 4] the one based on Roozeboom's freezing point (melting point)-composition diagrams has been employed to diagnose the nature of the racemic modification. If the diagram is composed of (i) three curves, it is a true *dl*-compound, (ii) two curves, it is a mechanical mixture or *conglomerate* and (iii) one curve, a solid solution of the optically active and opposite forms. We have characterised five of the compounds as true *dl*-compounds and the remaining four as solid solutions, whereas no case of a mechanical mixture has been observed. As the diagrams are symmetrical, only one of the active forms is required for the study.

EXPERIMENTAL

The preparation and the purification of the compounds have been described already.[5] The melting point-composition diagrams (Figs. 1–8) were prepared as given in our previous paper.[1] Tables giving melting points and percentage compositions have been omitted to economise space.

DISCUSSION

1. *Camphor-β-sulphonyl*-p-, m- *and* o-*nitrophenylamides*.—The melting point-composition diagram (Fig. 1 A) of the *para*-isomers consists of a single continuous curve with a maximum, which shows that the racemic form is a solid solution of the optically active and opposite forms. The melting point of the racemic form falls rapidly with the admixture of the *d*-form up to 50 per cent. and further admixture with *d*-form 60–100 per cent. hardly lowers

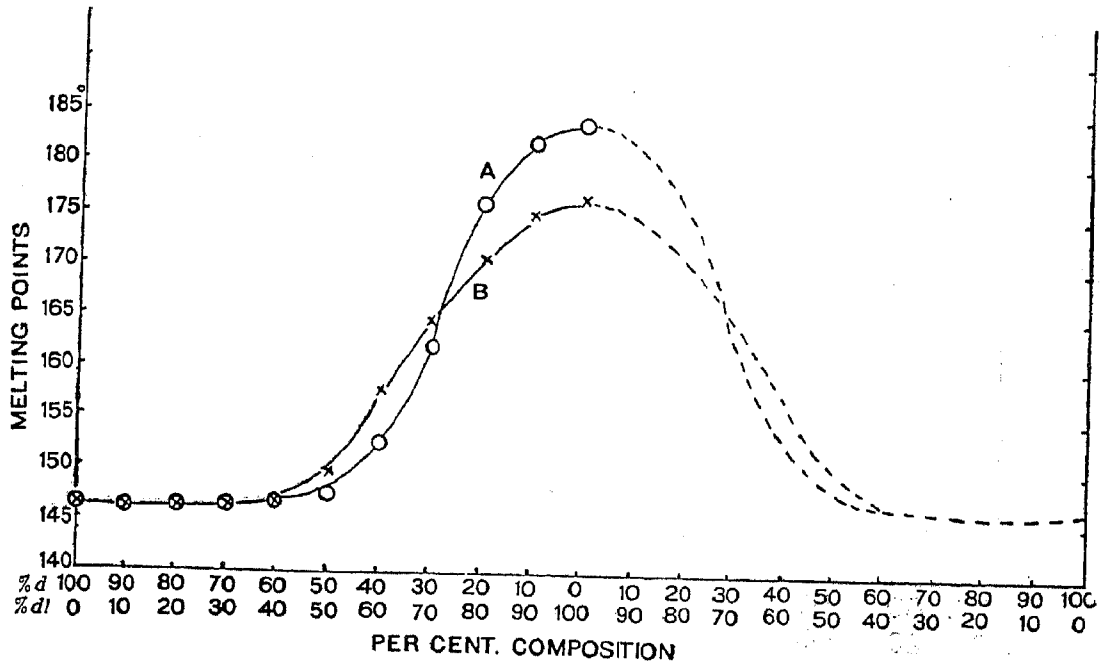

FIG. 1. A. Camphor-β-sulphonyl-*p*-nitro phenylamides O—O.
B. Camphor-β-sulphonyl-*m*-nitro phenylamides X—X.

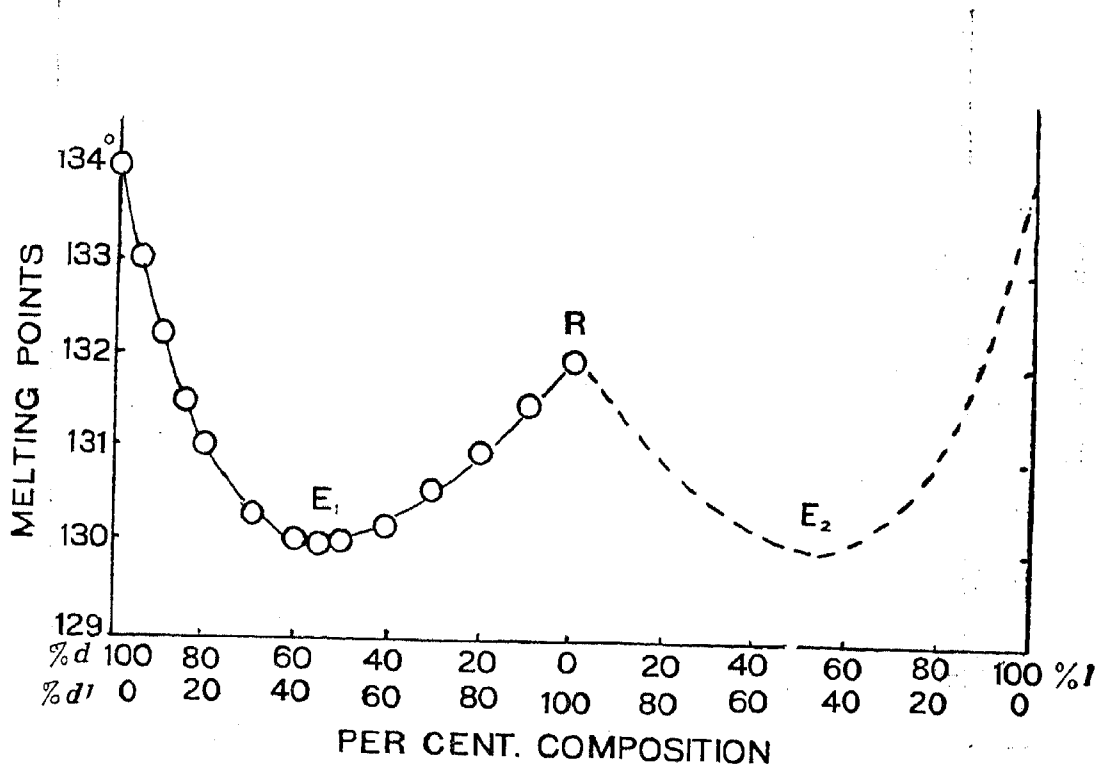

FIG. 2. Camphor-β-sulphonyl-*o*-nitro phenylamides.

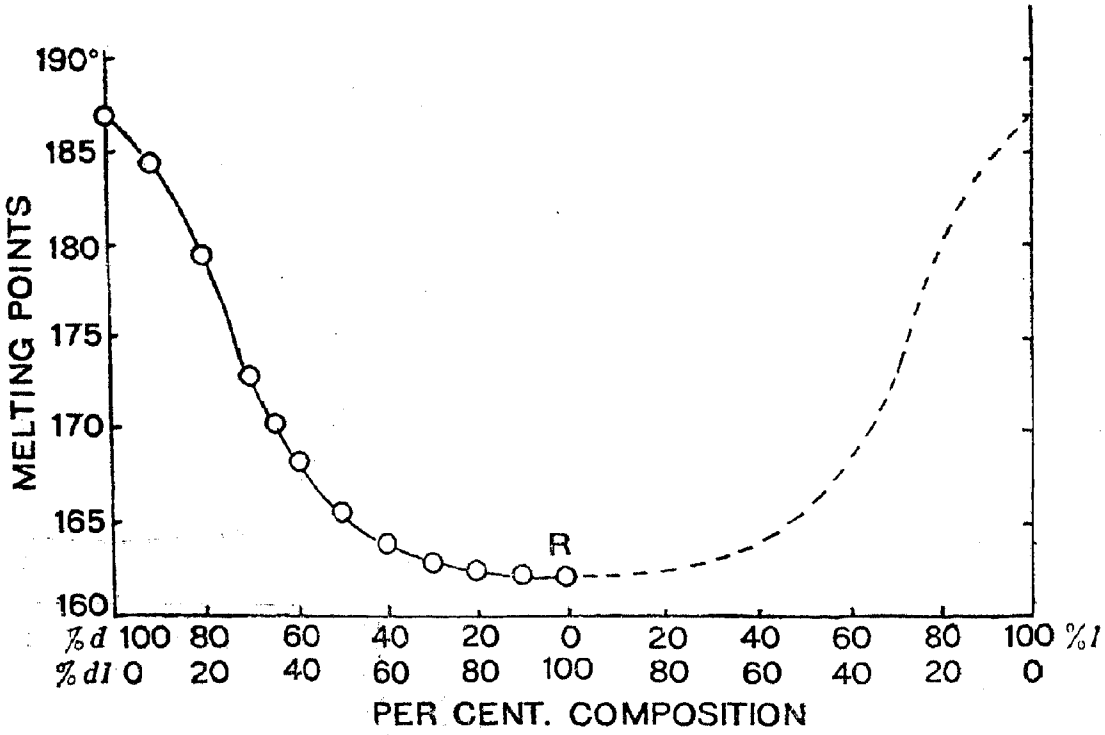

FIG. 3. Camphor-β-sulphonyl-*p*-phenylene diamines.

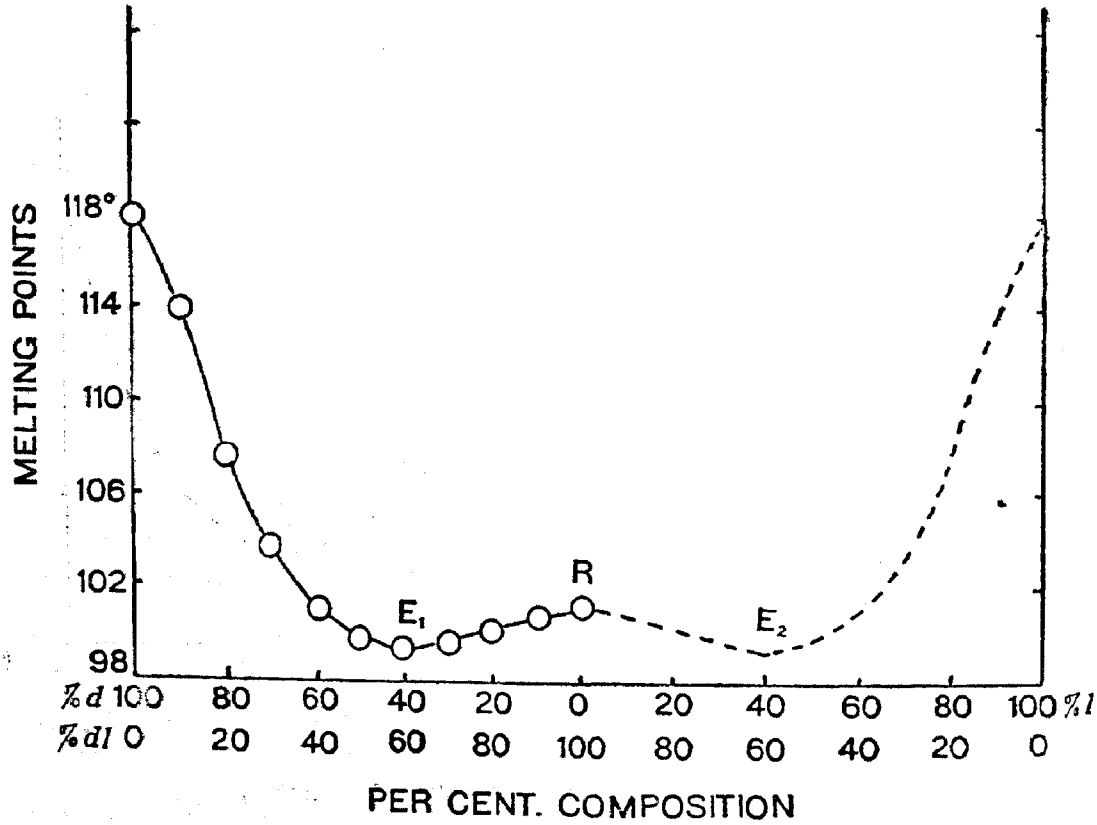

FIG. 4. Camphor-β-sulphonyl-*m*-phenylene diamines.

the melting point. The diagram (Fig. 1 B) of the *meta*-derivatives is very similar to that of the *para*-isomerides, consisting of only one continuous curve, which indicates the racemic form to be a solid solution. The melting point-composition diagram (Fig. 2) of *o*-isomerides consists of three curves with a central maximum R, which shows that the racemic form is a true *dl*-compound: *dl* - *d* and *dl* - *l* curves are fairly steep indicating that the racemic compound is stable and does not dissociate appreciably at its melting point. The central portion of the diagram does not occupy a large area, indicating its range of existence to be small. The eutectic points E_1 and E_2 are not sharp and well defined, indicating that in this region the active form and the racemic compound form solid solution.

2. *Camphor-β-sulphonyl*-p-, m- *and* o-*phenylenediamines.*—In the case of *meta* (Fig. 4) and *ortho* (Fig. 5) isomerides, the diagrams consist of three curves with a central maximum indicating the racemic forms to be *dl*-com-

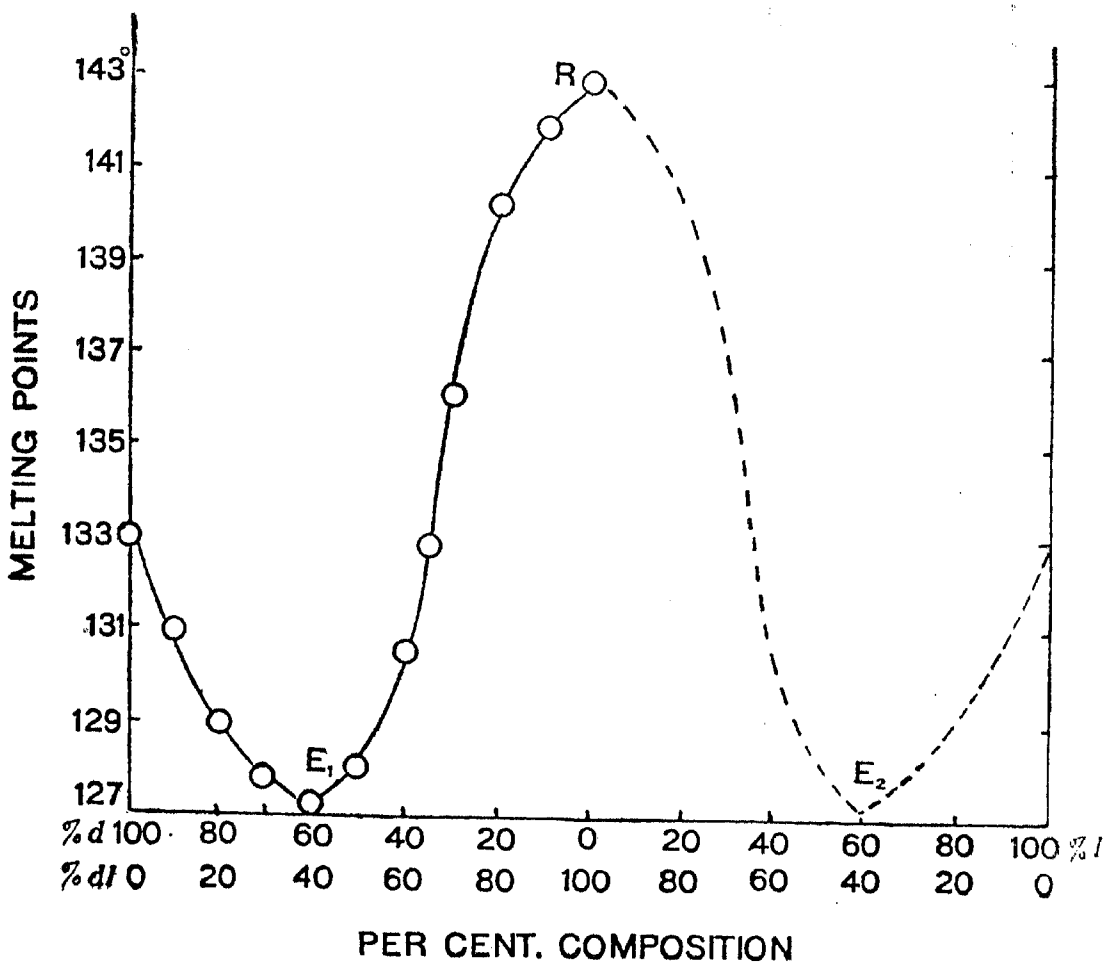

Fig. 5. Camphor-β-sulphonyl-*o*-phenylene diamines.

pounds. The central portion of the diagram for *m*-isomeride (Fig. 4) occupies a very small area and the eutectic points E_1 and E_2 are not sharp, indicating the low range of stability of the racemic form. On the other hand the central portion of the diagram in the case of the *o*-isomeride (Fig. 5) occupies a large area and the eutectic points are also well defined. This shows that the racemic form of the *o*-isomeride is more stable than that of the *meta*-isomeride. The steep fall of the curves, RE_1 and RE_2 (Fig. 5), indicates that the *ortho*-isomeride does not dissociate at its melting point. The melting point-composition diagram of the *para*-form (Fig. 3) has a minimum and the curve DRL, is continuous without any singular point, indicating the racemic form to be a solid solution.

3. p-, m- *and* o-*phenylene*-bis-*camphor-β-sulphonyl-amides*.—The melting point-composition diagrams of the *para* (Fig. 6) and *meta* (Fig. 7) iso-

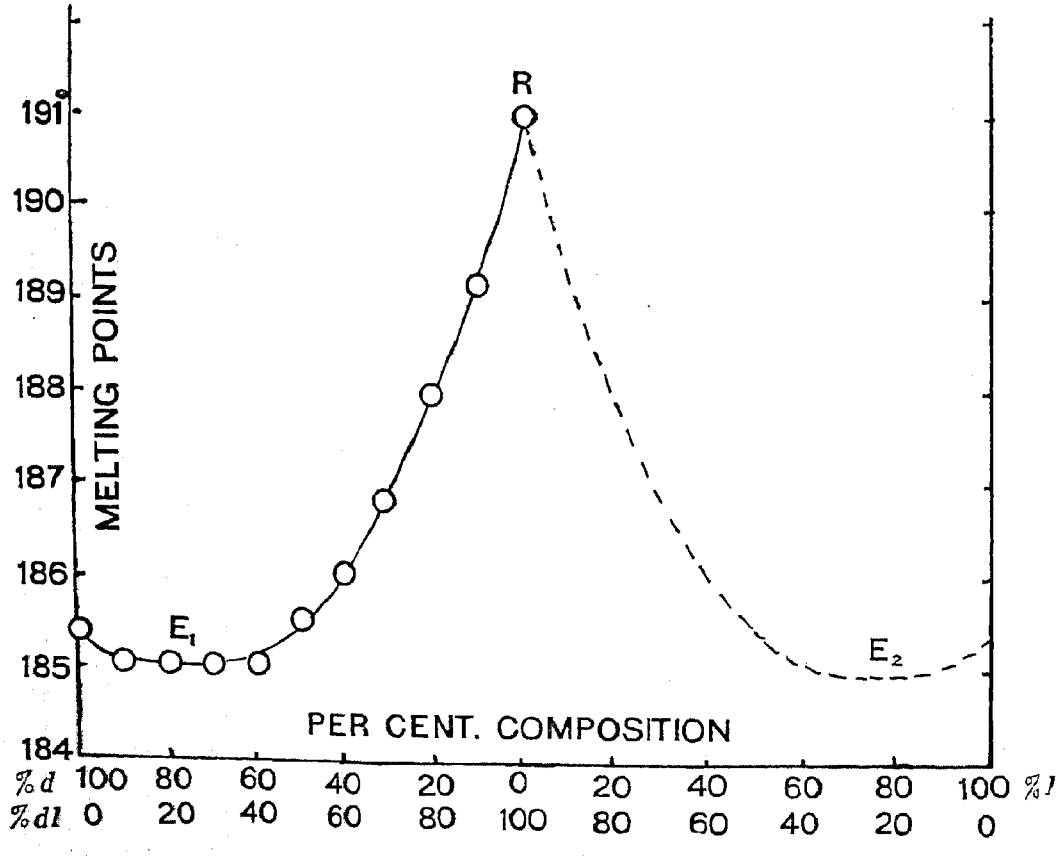

FIG. 6. *p*-phenylene-*bis*-camphor-β-sulphonyl amides.

merides show a central maximum and two eutectic points (E_1 and E_2). Each of them is composed of three curves DE_1, E_1RE_2 and E_2L, indicating the race-

mic forms to be true *dl*-compounds. In the case of *para*-isomerides (Fig. 6), the eutectic points are not sharp and well defined and the horizontal portion of the curve shows that the racemic compound forms solid solution with the *d*-form in the range between 90 per cent. *d*- to 60 per cent. *d*-isomerides. The steep curve, RE_1 shows that the racemic form is fairly stable. The diagram for the *meta*-isomerides (Fig. 7) has very sharp and well defined eutectic points; the curve, RE_1, is very steep, which indicates that the racemic compound is

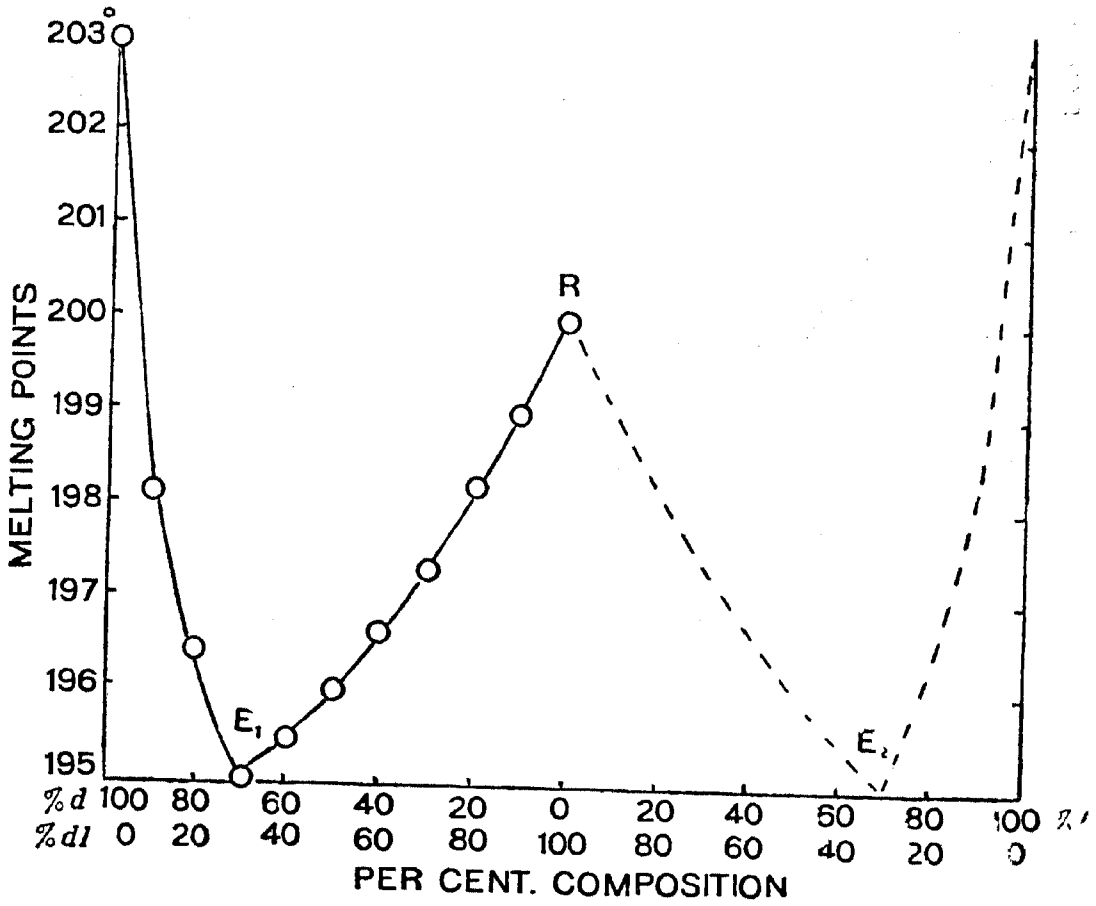

FIG. 7. *m*-phenylene-*bis*-camphor-β-sulphonyl amides.

very stable and does not dissociate at its melting point. Unlike *m*- and *p*-isomerides, the racemic form of the *o*-isomeride (Fig. 8) is a solid solution, which is evident from the continuous curve DE_1 RE_2L with a minimum. This curve is very similar to those obtained for *o*-chlorophenylimino and amino camphors[6] as well as camphor-β-sulphonyl-*p*-phenylenediamines described in this paper (Fig. 3).

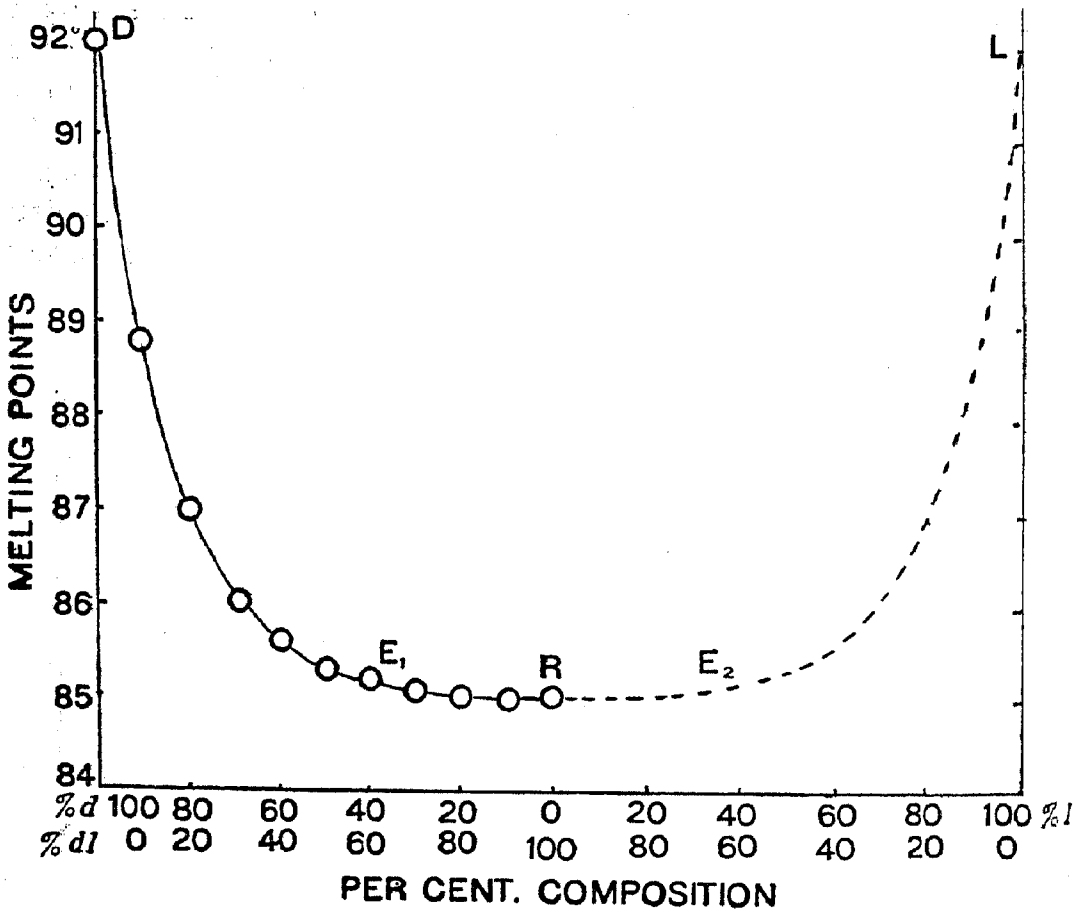

FIG. 8. *o*-phenylene-*bis*-camphor-β-sulphonyl amides.

SUMMARY

The nature of the racemic forms of the compounds has been investigated by the application of the melting point-composition method of Roozeboom. Out of the nine racemic forms, five have been found to be true *dl*-compounds varying in their stability and the remaining four form solid solutions. Two of the solid solutions, camphor-β-sulphonyl-*m*- and *p*-nitro-phenylamides give continuous curves with a maximum, while the remaining two, camphor-β-sulphonyl-*p*-phenylenediamines and *o*-phenylene-*bis*-camphor-β-sulphonyl-amides give continuous curves with a minimum.

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