16. *Isomorphous Relationships of Some Analogous Organic Derivatives of Oxygen, Sulphur, and Selenium.*

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Observations of temperature–concentration diagrams of binary mixtures of (a) diphenylene oxide, sulphide, and selenide, and (b) diphenylene dioxide, disulphide, and diselenide, have been made. The results are in harmony with the periodic relationships of the elements oxygen, sulphur, and selenium. For instance, in the former series it has been found that diphenylene sulphide and selenide and diphenylene oxide and sulphide yield continuous series of solid solutions, while diphenylene oxide and selenide exhibit only partial solid solubility.

The system diphenylene disulphide–diselenide shows that an unbroken series of solid solutions is present, whereas the systems diphenylene dioxide–disulphide and diphenylene dioxide–diselenide exhibit eutectics with negligible solid solution formation.

The spatial configurations of the molecules are discussed in the light of the above results.

THIS work was undertaken in order to ascertain if the isomorphous relationships of analogous derivatives of oxygen, sulphur, and selenium are in harmony with the periodic relationships of these elements. The series investigated were the following diphenylene derivatives: (*a*) oxide, sulphide, and selenide, and (*b*) dioxide, disulphide (thianthren), and diselenide (selenanthren), and the ability of binary mixtures of these compounds to form solid solutions was chosen as the criterion of isomorphism.

The only recorded investigation of this type is due to Pascal (*Bull. Soc. chim.*, 1912, **11**, 1030), who carried out similar experiments with diphenyl oxide, sulphide, and selenide. Of these substances, however, the last is unstable, and the purity of the specimen employed is in doubt (Drew and Landquist, J., 1935, 1482), whereas the compounds herein described are all quite stable, can be satisfactorily purified, and crystallise well.

Although recent investigations indicate that chemically dissimilar compounds may exhibit isomorphism provided that the shape of the space occupied by the molecules is similar (see, *e.g.*, Grimm, Günther, and Tittus, *Z. physikal. Chem.*, 1931, *B*, **14**, 169; Pirsch, *Ber.*, 1936, **69**, 1323; Lettré, Barnbeck, and Lege, *ibid.*, p. 1151), nevertheless substances of analogous chemical constitution possess geometrically similar molecules by virtue of this chemical similarity, and hence it may be concluded that the types of phase diagrams obtained in a series of compounds such as those now described are related to the chemical constitutions of the compounds.

Pascal's results (*loc. cit.*) show that, although diphenyl sulphide and selenide give a continuous series of solid solutions (type III, Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 385), only limited solid solubility is exhibited by diphenyl oxide and sulphide (type V) and by diphenyl oxide and selenide (type V).

That the spatial structures of the diphenyl oxide and conclude molecules are dissimilar is shown by the different values of the oxygen and sulphur valency angles in these compounds: Sutton and Hampson (*Trans. Faraday Soc.*, 1935, **31**, 945), from a consideration of electrical dipole-moment measurements, conclude that these angles are 128° ± 4° and 113° ± 3° respectively. The value of the selenium valency angle in diphenyl selenide is not known, but Pascal's results indicate that it is not far removed from that of the sulphur angle in diphenyl sulphide.

In the series diphenylene oxide, sulphide, selenide, the heterocyclic atoms form part of a rigid system in which therefore the oxygen, sulphur, and selenium valency angles probably differ less than in the corresponding diphenyl derivatives. The results show that diphenylene sulphide and selenide yield solid solutions in all proportions (Fig. 2; type I), as also do diphenylene oxide and sulphide (Fig. 1; type III), while diphenylene oxide and selenide possess limited solid solubility only (Fig. 3; type V). The closer resemblance between sulphur and selenium than between oxygen and selenium is thus confirmed.

The results obtained for the system diphenylene oxide–sulphide indicate a similarity in space structure agreeing with information furnished by dipole-moment measurements. The moment of furan is very small (*ca.* 0·65 D.; Hunter and Partington, J., 1931, **2066**; Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3234), and that of diphenylene oxide (dibenzofuran) is roughly of the same order (0·9; Bretscher, *Helv. Physica Acta*, 1929, **2**, 257), from which it may be inferred that the three rings in the latter compound are approximately coplanar, for any pronounced bending of the molecule, such as occurs, *e.g.*, in thianthren (Bennett and Glasstone, J., 1934, 128), would result in a considerable increase in the value of the moment. Thiophen and diphenylene sulphide (dibenzothiophen) present an analogous case. The moment of the former is *ca.* 0·6 (Hassel and Næshagen, *Tidsskr. Kjemi*, 1930, **10**, 81), and that of the latter is also not far removed from zero (Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 107). The dipole moments of selenophen and diphenylene selenide (dibenzoselenophen) are unknown, but the fact that diphenylene sulphide and selenide yield solid solutions in all proportions suggests that the molecules of these two compounds are similar in spatial configuration.

In the series diphenylene dioxide, disulphide, diselenide, we find that the last two compounds yield a continuous series of solid solutions (Fig. 5; type I), whereas the systems diphenylene dioxide–disulphide (Fig. 4) and –diselenide (Fig. 6) reveal a eutectic in each case with negligible solid-solution formation. The strong resemblance between sulphur and selenium and their dissimilarity to oxygen is thus confirmed. The absence of solid-solution formation in the first pair of the series is no doubt connected with the considerable difference in the spatial configurations of the molecules. Diphenylene dioxide has zero dipole moment (Bennett, Earp, and Glasstone, J., 1934, 1180), so that the molecule must be planar, and consequently the oxygen valency angles cannot be less than 120°, whereas in the case of the disulphide, the moment of which is 1·5 (Bennett and

Glasstone, *loc. cit.*; cf. Bergmann, *Ber.*, 1932, **65**, 463), the molecule is folded along a line passing through the sulphur atoms, and therefore the sulphur valency angles must be less than 120°. Although the dipole moment of diphenylene diselenide has not been determined, the evidence furnished by the present work indicates that its molecule also possesses a folded structure akin to that of thianthren.

The molecular volumes of thianthren and selenanthren were found to be very similar, and the close similarity of these compounds was further confirmed by crystallographic measurements (see p. 67).

EXPERIMENTAL.

Purification of Materials.—Some difficulty was experienced in preparing a sample of diphenylene oxide of sufficient purity for our purpose. A satisfactory specimen was finally obtained by fractional distillation, followed by three recrystallisations from dilute alcohol, and then two sublimations; it formed colourless scales, m. p. 82·4°.

Diphenylene sulphide was recrystallised from alcohol, then sublimed, and again similarly recrystallised; colourless needles, m. p. 98·9°. The selenide was recrystallised from alcohol, sublimed, and then distilled with steam. Further recrystallisation from alcohol afforded colourless needles, m. p. 71·0°.

Diphenylene dioxide, purified by distillation with steam, recrystallisation (twice) from alcohol, and finally sublimation, formed long, thin, colourless needles, m. p. 119·7°. The disulphide was distilled under diminished pressure, followed by sublimation and recrystallisation (thrice) from acetone; the pure product consisted of colourless needles, m. p. 156·7°. Purification of diphenylene diselenide was effected by distillation under reduced pressure, followed by repeated recrystallisation from acetone; colourless needles, m. p. 179·4°.

Method of Experiment.—Thaw points (T_1) and melting temperatures (T_2) were determined by the method of Rheinboldt and Kircheisen (*J. pr. Chem.*, 1925, **111**, 246; 1926, **113**, 348), the determinations being carried out in small capillaries. Temperatures were recorded on a small Anschütz thermometer graduated to 0·1°, which had been standardised at the National Physical Laboratory. For each system investigated determinations of T_1 and T_2 were made under exactly similar conditions. Values of T_1 could be reproduced to within 0·2°, and those of T_2 to within a narrower range. For the pure compounds, T_1 and T_2 did not differ by more than 1°.

The results are shown graphically in Figs. 1—6, and the complete data are tabulated below.

System Diphenylene Oxide–Diphenylene Sulphide (*Fig.* 1).

Sulphide, mols. %	0	8·1	13·5	23·2	41·6	49·9	66·7	84·2	100
T_1	81·7°	81·1°	80·8°	80·4°	80·6°	81·5°	83·3°	88·0°	98·4°
T_2	82·4	81·9	81·1	80·6	81·4	82·5	85·6	91·6	98·9

The curve is very unusual, inasmuch as the maximum depression of the m. p. is only 1·8°, corresponding to 26 mols. % of sulphide.

System Diphenylene Sulphide–Diphenylene Selenide (*Fig.* 2).

Sulphide, mols. %	0	7·6	19·9	48·1	76·0	85·6	100
T_1	70·0°	70·1°	71·0°	75·2°	83·2°	87·5°	98·4°
T_2	71·0	72·2	75·9	85·0	94·0	95·7	98·9

The m. p.'s of all mixtures lie between those of the pure components.

System Diphenylene Oxide–Diphenylene Selenide (*Fig.* 3).

Oxide, mols. %	0	10·2	17·3	26·1	32·7	34·1	39·2	57·0	69·2	80·8	100
T_1	70·0°	56·2°	51·8°	51·7°	51·6°	51·0°	51·3°	51·7°	54·9°	61·8°	81·7°
T_2	71·0	66·1	63·8	59·5	56·6	56·0	57·7	64·9	70·2	74·6	82·4

The system reveals a eutectic at 53°, corresponding to 35 mols. % of oxide, the compositions of the solid solutions being *ca.* 15 and 63 mols. % of oxide.

System Diphenylene Dioxide–Diphenylene Disulphide (*Fig.* 4).

Dioxide, mols. %	0	5·2	9·0	19·3	42·3	56·0	63·1
T_1	156·1°	101·7°	101·8°	101·8°	101·6°	101·6°	101·6°
T_2	156·7	154·7	153·0	147·8	134·2	123·8	117·2
Dioxide, mols. %	71·1	72·2	78·9	87·7	92·6	96·0	100
T_1	101·7°	101·7°	101·6°	101·9°	101·8°	101·5°	118·8°
T_2	102·8	104·7	109·0	113·8	116·2	117·7	119·7

The curve shows a simple eutectic, with no solid solution formation. The eutectic point is 101·6°, corresponding to 69·5 mols. % of dioxide.

FIG. 1.

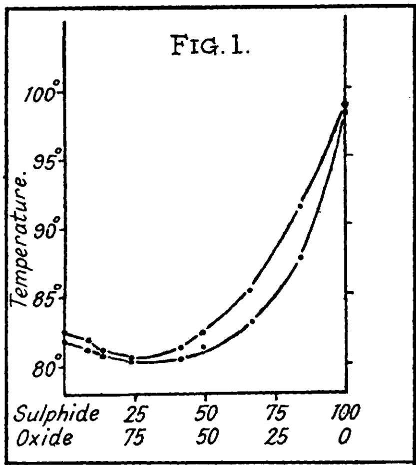


FIG. 2.

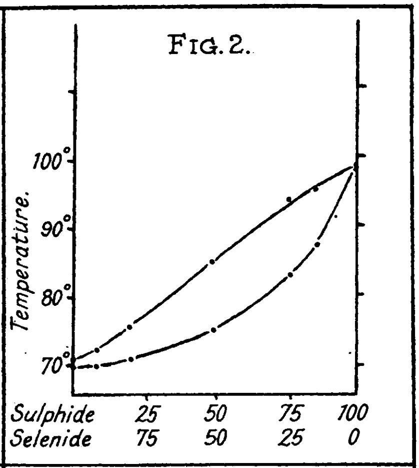


FIG. 3.

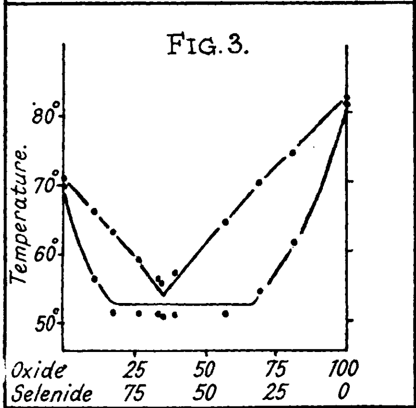


FIG. 4.

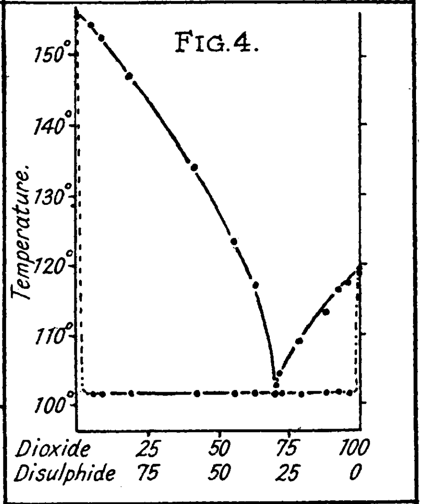


FIG. 5.

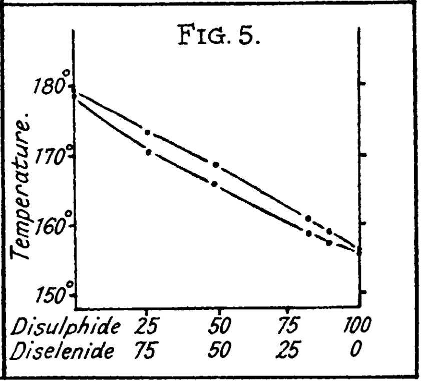
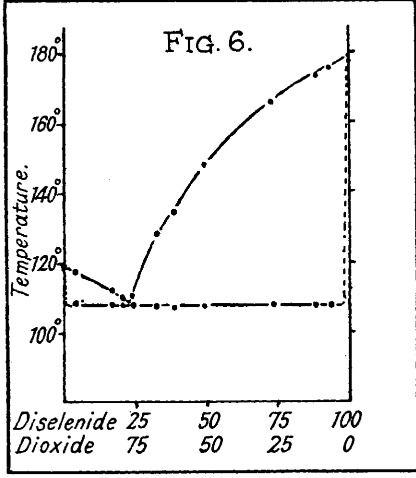


FIG. 6.



Legends to abscissæ give mols. %.

System Diphenylene Disulphide–Diphenylene Diselenide (*Fig.* 5).

Disulphide, mols. %	0	25·6	49·1	81·9	89·3	100
T_1	178·8°	170·6°	166·0°	159·0°	157·8°	156·1°
T_2	179·4	173·7	168·8	161·0	159·2	156·7

The m. p.'s of all mixtures lie between those of the pure components.

The densities and molecular volumes are as follows: Disulphide, $d = 1{\cdot}43$, mol. vol. $= 151$. Diselenide, $d = 1{\cdot}92$, mol. vol. $= 160$.

Both solids crystallise in the monoclinic system, the axial ratios and angle being as follows (private communication from Messrs. R. G. Wood and J. E. Crackston of the Physics Department of this College):

Disulphide, $a : b : c = 2{\cdot}34 : 1 : 2{\cdot}47$; $\beta = 132° 22'$.

Diselenide, $a : b : c = 2{\cdot}40 : 1 : 2{\cdot}53$; $\beta = 132° 59'$.

A complete crystallographic and *X*-ray study of these substances will be published elsewhere.

System Diphenylene Dioxide–Diphenylene Diselenide (*Fig.* 6).

Diselenide, mols. %	0	2·9	16·6	20·4	23·8	32·1
T_1	118·8°	108·4°	108·1°	108·1°	108·0°	108·0°
T_2	119·7	118·7	112·5	110·5	111·2	129·6
Diselenide, mols. %	38·3	49·5	73·3	88·3	93·6	100
T_1	107·9°	108·2°	108·2°	108·2°	108·3°	178·8°
T_2	135·8	148·6	167·0	174·5	176·6	179·4

The system forms a simple eutectic at 108·2°, with no solid solution formation, corresponding to 77 mols. % of dioxide.

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