CLXXIX.—*Studies of Dynamic Isomerism. Part XXVII. The Absorption Spectra of Prototropic Compounds. Physical Properties of the Stable and Labile Forms of Benzoylcamphor.*

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IN a paper on " Absorption Spectra and Tautomerism " (J., 1926, 706), Morton and Rosney put forward the view " that enolic and ketonic modifications possess the same wave-length of maximum absorption." As evidence in support of this conclusion they cite " the facts that addition of alkali to acetone (which presumably gives rise to a trace of an enolic salt) increases the intensity of the band, but does not produce a new band, and that the *two isomeric forms of benzoylcamphor give bands at the same wave-length, but of unequal intensity* " (p. 709). The theoretical conclusion of these authors appears to us to be very plausible, since two isomerides, which are so nearly on the same energy level that they can exist in dynamic equilibrium with each other, might very well have similar energies of activation, and therefore absorb light of similar wave-length. The observations on which they rely are, however, of a much less satisfactory character. In particular, the action of an alkali in intensifying the selective absorption of acetone is capable of alternative explanations (see especially Dawson's work on the catalysis of the iodination of acetone by acids and alkalis) and is therefore of little value as evidence in support of their conclusion; and, in the case of benzoylcamphor, the " facts " cited by the authors are in direct contradiction to measurements which had already been made by us, and which were communicated to Dr. Morton, prior to the publication of his paper. We were therefore in a position to challenge his conclusions immediately, on the basis of perfectly trustworthy data ; but, in view of the obvious incompatibility of the two sets of data, we thought it wise to postpone our criticisms until we had repeated and confirmed all our observations, and moreover had extended them in other directions to such a point that we were absolutely satisfied of their validity.

The choice of benzoylcamphor as a material for tests of this kind is justified by the exceptional stability of its two forms, which undergo isomeric change so slowly that a complete pseudobinary fusion-point diagram can be plotted for them (Vixseboxse, *Rec. trav. chim.*, 1921, **40**, 1). For the present purpose, however, where the homogeneity of the two isomerides is of crucial importance, the fact that both forms have been isolated in measurable crystals is of still greater value, since this provides an even more certain guarantee of the individuality of the preparations and of their freedom from all but isomorphous impurities. The purity of the two forms can also be checked by measurements of their initial rotatory powers in an inert solvent, as well as by the more usual method of observing their melting points when they are heated at such a rate as not to allow isomeric change to precede the melting of the compound.

The constitutions of the two forms need only be referred to incidentally, since none of the experimental data now recorded would be affected in any way if it could be shown (as Lapworth has already suggested to one of us in the case of nitrocamphor) that the two dominant forms are stereoisomeric. The structures originally assigned to them by Forster, on the basis of the ferric chloride test, have, however, been vindicated by the later work of Dimroth and of Vixseboxse, who have shown that the "enol" can be titrated sharply by Kurt Meyer's method, and that this method gives values for the equilibrium proportions of the two forms which are identical with those deduced from the optical rotations of the solutions. In the present paper, therefore, we have made use of Forster's nomenclature, and have referred to the stable and labile forms of the compound as enolic and ketonic, respectively.

The known forms of benzoylcamphor represent only two of the five theoretically possible isomerides. It is, however, unlikely that any other isomeride plays an important part in the equilibrium, since (i) the mutarotation curves are at least approximately unimolecular (see J., 1923, **123**, 2122), (ii) the percentage of enol deduced by Dimroth and Vixseboxse from bromine titrations, and by ourselves from the ratio of the initial and final solubilities of this form (p. 1344), is identical with that calculated from the optical rotatory power of the equilibrium mixture.

The measurements of absorption now described were made as part of an extensive study of the physical properties of the stable and labile forms of benzoylcamphor, which required that we should prepare a considerable number of samples of each isomeride and satisfy ourselves at every stage that the material consisted exclusively of one or other form of the compound. Thus the earlier observations, which were communicated to Dr. Morton, were made in the course of an investigation in which we sought to establish also (i) the unimolecular character (or otherwise) of the mutarotation curves (*loc. cit.*, 1923) and (ii) the form of the curves of rotatory dispersion of the two isomerides, by extrapolation to zero time of the observed rotations for different wave-lengths. In the same way, the second series of experiments (which was undertaken primarily in order to confirm the earlier results) included the determination of (iii) the melting points of the two isomerides under specified conditions, (iv) the initial and final rotations of the two forms, in order to calculate the equilibrium proportions of ketone and enol in three different solvents, (v) the initial solubilities of the unchanged isomerides in these solvents, in order to test van 't Hoff's activity formula, and (vi) the initial and final solubilities of the stable enolic form, in order to determine the proportion in which it is present in the final equilibrium mixture. The numerical results of these investigations are summarised in Table I.

TABLE I.

Physical Properties of Benzoylcamphor.

	Enol.	Ketone.	Equilibrium mixture.	Equilibrium proportion of enol.
Melting point	89·5°	112°	84°	—
Specific rotation $[\alpha]_{5461}$				
in alcohol	331°	152°	258°	59%
in acetone	339°	145°	248°	53%
in benzene	315°	50°	257°	78%
Rotatory dispersion $\alpha_{4358}/\alpha_{5461}$				
in benzene at 20°	2·393	1·555	—	—
Solubility (g./100 g. solution)				
in alcohol at 17°	3·37	2·95	5·83*	58%
in acetone at 17°	19·0	19·3	36·4*	52%
in benzene at 17°	37·3	16·9	43·1*	87%
Molecular extinction coefficient				
in alcohol (M/10,000)			$\log \epsilon$	
1st series λ =	3120	2475	3·95 3·80	
$\log \epsilon$ =	4·19	4·06		
2nd series λ =	3140	2420	4·10 3·90	66%
$\log \epsilon$ =	4·27	4·21		69%

* Solid phase, the enol.

EXPERIMENTAL.

Preparation of Materials.—The work now described was delayed for many months because the published directions for making the intermediate dibenzoyl derivative failed, in the hands of later workers, to give even the moderate yields (about 8% of the weight of camphor) which had been obtained previously. This failure was ultimately traced to the excessive care that was used to prevent the benzoylation from getting beyond control. The revised directions which have rendered the product once more available in reasonable quantities are therefore set out below, together with the methods used in preparing colourless and homogeneous samples of enolic and ketonic benzoylcamphor.

(a) *Benzoyloxybenzoylcamphene.* Flowers of camphor (150 g.) were dissolved in toluene (400 c.c.) which had been dried over sodium wire. Sodium (15 g.) was added, preferably in one piece, and heated in a flask on a water-bath under a condenser until the sodium began to melt. The flask was then removed and shaken vigorously to start the action, which was controlled by dipping the flask in ice-water. When the reaction had finished, the liquid was poured into a wide-necked bottle, which was then surrounded with ice. Benzoyl chloride (75 g.) was added in small portions, with continuous and thorough stirring by means of a glass rod, at such a rate that the temperature of the mixture remained between 25° and 28°. The product, which had the colour and consistency of vaseline, was allowed to stand for 2 hours, and then shaken several times with cold water, until the latter no longer became coloured. The toluene was recovered by distillation from a water-bath, under a pressure of about 120 mm., and the last traces of solvent were removed by reducing the pressure to 15 mm. The syrupy residue was steam-distilled until the smell of camphor could no longer be detected. If the aqueous layer deposited crystals of benzoic acid on cooling (which does not occur in a correct preparation), the syrup was freed from this acid by shaking several times with boiling water. When quite cold it was separated as far as possible from water, and just half its volume of 96% alcohol was added. After 20 hours the crystals of benzoyloxybenzoylcamphene, which in a correct preparation are already colourless, were filtered off and recrystallised from boiling alcohol.

(b) *Benzoylcamphor* (*enolic form*). The dibenzoyl compound (10 g.) was dissolved in alcohol (100 c.c.) and heated on a water-bath for 2 hours under reflux with a solution of sodium hydroxide (2·3 g. of sodium) in alcohol (25 c.c.) to which a little water (4 c.c.) had finally been added. The alcohol was distilled off, the last traces being removed by adding and distilling off a little water. The solid residue of sodium salts was dissolved to a cloudy solution by shaking three times with water (3 × 500 c.c.) at 80°. Colourless benzoylcamphor was then precipitated by passing carbon dioxide into the cold filtered solution. The red tinge, which is developed when boiling water is used to dissolve the sodium salt, may be removed by dissolving the product in ether, shaking twice with water, twice with dilute hydrochloric acid (1 : 1), and again with water. The crude benzoylcamphor was crystallised from cold ether (in which solvent the equilibrium mixture contains 84% of enol) by evaporation under reduced pressure, and separated in highly refracting, colourless prisms. Further purification was effected by dissolving the compound in boiling light petroleum (or heptane) and stirring with a glass rod which had been exposed to the fumes from concentrated hydrochloric acid; the crystals, which separated slowly on cooling, were crushed and washed with ether containing a trace of hydrogen chloride.

(c) *Benzoylcamphor* (*ketonic form*). The ketonic form of benzoylcamphor was prepared by heating the enolic form (10 g.) under reflux with concentrated formic acid (20 c.c.) for 4 hours (compare Dimroth, *Annalen*, 1913, **399**, 110). After cooling (and without filtering, because there was nothing to filter), the liquid was shaken for 3 minutes with light petroleum. The precipitated crystals were drained on a Büchner funnel, washed quickly with light petroleum, shaken with water, drained, washed until all traces of formic acid had been removed, and finally dried in a vacuum over sulphuric acid. If desired, they can be recrystallised by dissolving them in ether at 20° and evaporating a part of the solvent under reduced pressure; but it was found that the melting point of the product was often lowered instead of being raised by this further treatment.

Melting Points.—Melting points of the two forms of benzoylcamphor have been given by earlier workers as follows :

	Forster.	Dimroth.	Vixseboxse.
Enol	89°	90—91°	89°
Ketone	87—88	112	107

The triple point, at which the enol crystallises from the molten equilibrium mixture, is 84°. After fusion, therefore, any chemically pure sample of benzoylcamphor will freeze at this temperature, and the melting points of both forms will tend to the same value if time is allowed for isomeric change to occur before fusion. It was therefore important to know what is the minimum time in which a melting-point tube can be heated, and its contents fused, when the temperature of the bath is higher than the melting point by a known amount. In order to obtain this information, purified acetanilide, in a fine melting-point tube, was plunged into a bath heated to different temperatures, and was found to melt in over 60 seconds with the bath at 113·9°, in about 40 seconds at 114·0°, and in about 15 seconds at 114·1° and above. These experiments show that fusion cannot be effected in less than about 15 seconds when the melting-point tube is plunged into a bath at a slightly higher temperature, but that the lowest bath-temperature at which fusion takes place within this time is only about 0·2° above the true melting point. Under these conditions the enolic form of benzoylcamphor melts at 89·5° and the ketone at 112°. The latter temperature agrees with the melting point given by Dimroth, but, if a period of 1 minute instead of ¼ minute is allowed for fusion, the melting point is lowered by perhaps 5°, and therefore corresponds roughly with that recorded by Vixseboxse.

The melting point given by Forster is only a little above the triple point; but this might easily be recorded as the melting point, if determined in the ordinary way, without making use of the special precautions that are needed in the case of a labile compound. For instance, when a single crystal of a sample which melted at 112° was crushed on a porous plate and heated in a melting-point tube, it melted within a minute at 90°. The substantial homogeneity of Forster's material is proved, however, by the fact that the initial rotations recorded for solutions in alcohol and in chloroform are very similar to those given in the present paper; and the complete identity of his labile material with ours is proved by the facts that the crystals belong to the same system, exhibit the same faces, and have the same axial ratios within the limits of experimental error, namely $a : b : c = 0{\cdot}7375 : 1 : 1{\cdot}0224$ (Forster) $= 0{\cdot}7454 : 1 : 1{\cdot}0138$ (L., McC., and B.).

Anthes's melting-point apparatus (*Chem.-Ztg.*, 1911, 1375), in which the liquid of the bath is made to circulate through a lateral heating-tube, was used for these experiments, but greater uniformity of temperature was secured by heating electrically instead of by a flame. For this purpose the heating-tube was wound with resistance wire and covered with Pyruma cement. The apparatus was protected from draughts by a little cardboard box with glass front and back, holes being provided in the sides of the box for the two side tubes through which melting-point tubes were immersed in the bath. When paraffin oil or concentrated sulphuric acid was used, the circulation was slow, on account of the viscous nature of the liquid; xylene (b. p. 133°), which is very mobile at 110°, was therefore used, and gave a rapid circulation and uniform heating of the thermometer. The temperature rose quickly when a heating current of about 0·5 amp. was used, and could be regulated easily to 0·1°.

Optical Rotations.—The following values have been found for the initial and final specific rotations $[\alpha]_{5461}$ of the two forms in three typical solvents ($c = 1{\cdot}25\%$ in each case).

	Enol.		Ketone.		Equilibrium mixture, %.	
Solvent.	Initial.	Final.	Initial.	Final.	Enol.	Ketone.
Alcohol	331°	258°	152°	258°	59	41
Acetone	339	248	145	249	53	47
Benzene	315	256	50	257	78	22

It will be seen that the rotatory power of the enolic form is very similar in all three solvents, but that the ketone has a much lower rotatory power in benzene than in acetone or alcohol. A similar contrast is seen in the proportions of enol and ketone in the equilibrium mixture, which show clearly that the two oxygenated solvents favour the formation of the ketone in a much higher degree than does the hydrocarbon. The correlation of this displacement of equilibrium with the relative solubilities of the ketone and enol in the three solvents is discussed below.

Rotatory Dispersion.—The rotatory dispersions of the enolic and ketonic forms of benzoylcamphor were measured in 6-dcm. tubes at 20° in pure benzene. The concentrations of the solutions were as follows :

Enolic benzoylcamphor, 8·000 g. in 52·242 g. of solution :

$d_{4^\circ}^{20^\circ} = 0{\cdot}9075$, hence $c = 13{\cdot}90$ g./100 c.c. : $[\alpha] = 1{\cdot}199\ \alpha$.

Ketonic benzoylcamphor, 8·000 g. in 61·7075 g. of solution :

$d_{4^\circ}^{20^\circ} = 0{\cdot}9034$, hence $c = 11{\cdot}71$ g./100 c.c. : $[\alpha] = 1{\cdot}423\ \alpha$.

Since each form changed into the other during the determinations, the observed rotations had to be corrected in order to give the rotatory power of the pure compounds. For this purpose the rotation of each form for the line Hg 5461 was measured at intervals during the experiment and plotted against the time. The amount of ketone and of enol present at the time of each determination could be read off from the graph and the rotation of each form at zero time could then be calculated. In the case of the enol, the correction, even of the latest readings, is probably accurate within ± 0·5° ; that of the earliest readings, *e.g.*, those taken with the mercury lines, is proportionally more exact. In the case of the ketone, the error from this source should not be larger than 0·1° for the three mercury lines, which were read first, and about 0·25° for two copper yellow lines and the zinc red line, which were read next, but the solution had then changed so much that no further readings were taken; the values used to correct the rotations of the enolic form were therefore interpolated from a curve of rotatory dispersions, on which the rotations of the mercury lines and the zinc red line were plotted. The observed and corrected rotations are set out in Table II, together with values for the specific rotation of the enolic form, calculated from the formula

$$[\alpha] = \frac{80 \cdot 82}{\lambda^2 - 0 \cdot 10023} - \frac{27 \cdot 65}{\lambda^2}.$$

The rotatory dispersion of enolic benzoylcamphor can be expressed quite satisfactorily by means of a three-constant formula, since, even on specific rotations of several hundred degrees, the difference between the (corrected) observed and calculated values is always less than a degree. Since the second dispersion constant is ignored in a three-constant equation, the value of the first dispersion constant is not very trustworthy; but the characteristic wave-length, $\lambda = 3160$, deduced from the equation agrees closely with the observed head of the absorption band at 3100 or 3140 Å.U. It is, moreover, noteworthy that the difference is similar in direction to, although substantially smaller in magnitude than, that which has already been recorded in camphorquinone and in camphor, where it amounts to about 70 Å.U. (J., 1924, **125**, 2521; 1925, **127**, 611), as well as in the halogen derivatives of camphor, which produce a much stronger " general absorption " than camphor and give a discrepancy of about 140 Å.U. The same explanation of the discrepancy may therefore be adopted, namely, that " when a selective absorption is superposed on a strong general absorption, the observed head of the band will be displaced to a region of shorter wavelengths " (J., 1925, **127**, 1267).

The rotatory dispersion of the ketone is in striking contrast with that of the isomeric enol. Thus the rotation of the enol increases rapidly as the wave-length decreases, and tends towards an infinite positive value at the absorption band; moreover, since the rotation constant of the positive low-frequency term is three times as great as that of the negative high-frequency term, the rotation must remain positive over the whole range of wave-lengths, the rotatory dispersion being therefore " complex but normal." In accordance with this behaviour the dispersion ratio $[\alpha]_{4358}/[\alpha]_{5461}$ of the enol is as high as 2·393; that of the ketone, on the other hand, is only 1·555. The latter value agrees closely with the theoretical ratio 1·57 for a substance obeying Biot's law of inverse squares, $\alpha = k/\lambda^2$, where k has the value 18·04. In this respect, therefore, the rotatory dispersion of the ketone is similar to that of sodium tartrate (Lowry and Austin, *Phil. Mag.*, 1922, *A*, **222**, 249) and of octyl oxalate (Lowry and Richards, J., 1924, **125**, 1596). Since, however, this value for the dispersion ratio could only be reached if the nearest absorption band were at zero wave-length (and smaller values would make the characteristic wave-length an imaginary quantity), it is evident that the apparent simplicity of the dispersion law is only an approximation resulting from a balancing of two partial rotations of opposite sign. In the two cases cited above, this complexity was made obvious by small, systematic deviations from the calculated rotations; in the present instance there are not enough data to show these small deviations, but, since the dispersion ratio is actually less than the theoretical minimum, it is clear that the rotations can only be expressed by a two-term equation, with terms of opposite sign. It can, indeed, be predicted with some confidence that the rotatory dispersion would become anomalous in the ultra-violet region, and undergo a reversal of sign as the ketonic absorption band at $\lambda = 2480$ Å.U. is approached, since this predicted anomaly has already been verified experimentally in the case of sodium tartrate.

TABLE II.

Rotatory Dispersion of Benzoylcamphor in Benzene at 20°.

	(*a*) Ketonic form.				(*b*) Enolic form.					
Wave-length.	t (min.).	$[\alpha]$ (obs.).	Correction.	$[\alpha]$ (corr.).	t (min.).	$[\alpha]$ (obs.).	Correction.	$[\alpha]$ (corr.).	$[\alpha]$ (calc.).	Diff.
Cd 6438	—	—	—	+*42·2* *	241	+188·72	+1·90	+190·6	+190·4	+0·2
Zn 6362	116	+45·97	−2·17	+42·8	53	196·79	0·25	197·0	197·1	−0·1
	91	+44·84	−1·54	+43·3						
Na 5893	—	—	—	+*51·3*	—	—	—	*255·6*	—	—
Cu 5782	105	+57·31	−3·21	+54·1	111	261·58	0·90	262·5	262·5	±
Hg 5791	75	+54·29	−0·99	+53·3	28	262·65	0·16	262·8	262·8	±
Hg 5770	54	+53·65	−0·25	+53·4						
Cu 5700	110	+58·85	−3·95	+54·9	117	274·17	1·00	275·2	274·6	+0·6
Ag 5465	—	—	—	+*60·2*	228	311·78	2·95	314·7	314·6	+0·1
Hg 5461	49	+60·77	−0·27	+60·5	46	315·22	0·29	315·5	315·5	±
Cu 5218	—	—	—	+*67·2*	73	367·44	0·75	368·2	368·2	±
Cu 5153	—	—	—	+*69·2*	84	384·11	0·95	385·0	384·7	+0·3
Cu 5106	—	—	—	+*70·6*	95	395·61	1·15	396·8	397·7	−0·9
Cd 5086	—	—	—	+*71·4*	258	398·48	4·69	403·2	403·2	±
Zn 4811	—	—	—	+*81·0*	68	495·47	0·94	496·4	496·6	−0·2
Zn 4722	—	—	—	+*84·3*	123	532·26	2·20	534·5	534·4	+0·1
Hg 4358	62	+95·52	−1·42	+94·1	37	753·77	0·72	754·5	755·2	−0·7
Hg 5461	66	+61·19	—	—	24	315·16	—	—	—	—
,,	82	+62·29	—	—	139	314·05	—	—	—	—
,,	163	+71·98	—	—	148	313·81	—	—	—	—
,,	174	+73·84	—	—	188	313·31	—	—	—	—
,,	—	—	—	—	198	313·10	—	—	—	—
,,	—	—	—	—	308	310·26	—	—	—	—
,,	—	—	—	—	321	310·17	—	—	—	—

* Extrapolated or interpolated values are shown in italics.

Solubilities.—When dissolved in an inert solvent of reasonable purity, and at a low temperature, the two forms of benzoylcamphor are converted into each other so slowly that it is possible to measure, not only the solubility of the stable form before and after isomeric change has taken place (as described in Parts II and III of this series, J., 1904, **85**, 1541, 1551), but also the initial solubility of the labile ketonic form. Benzoylcamphor was therefore selected by Dimroth (*Annalen*, 1913, **399**, 110) as a suitable substance with which to test the theorem of van 't Hoff, that the change of equilibrium due to the solvent is completely allowed for when " the unit of concentration is no longer the gram-molecule per litre, but the concentration of the saturated solution " ("Vorlesungen," 1898, I, 217; English trans., p. 221), or, as Dimroth expresses it, " two interchangeable isomers, desmotropes or tautomers are in equilibrium in any solvent, when their concentrations are in the same proportions to one another as their solubilities in that solvent, multiplied by a constant G." Thus $c_A/l_A = G \times c_B/l_B$, or $c_A/c_B = G \times l_A/l_B$, where c_A and c_B are the concentrations, and l_A and l_B the solubilities of the two forms in a given solvent, and G is a function of the vapour pressures of the two forms and of their equilibrium concentrations in the vapour, but is independent of the solvent.

Van 't Hoff's theorem (which does not allow of a reversal of solubility by change of solvent) is obviously not applicable in the case of *iso*nitrosomalonanilide, which crystallises from alcohol, ether, ethyl acetate, or acetic acid in white, pearly scales, but from chloroform or benzene in yellow needles (Whiteley, J., 1903, **83**, 34), nor in the case of nitroformaldehydehydrazone, which separates in the α-form from benzene, chloroform, or light petroleum, but in the β-form from water or alcohol (Bamberger, *Ber.*, 1901, **34**, 2001). Dimroth, however, found the following ratios for the two forms of benzoylcamphor at 0°, and concluded that " van 't Hoff's theorem is completely confirmed."

	c_A/c_B.	l_A/l_B.	G.
Ether	6·81	6·39	1·06
Ethyl acetate	1·98	1·81	1·09
Ethyl alcohol	1·67	1·57	1·06
Methyl alcohol	0·87	0·748	1·15
Acetone	0·853	0·80	1·06

Vixseboxse, on the other hand, after measuring the concentration ratios and the solubility ratios in three solvents at 17°, found that the value of G varied from 1·13 to 1·52, and concluded that " G is therefore not constant " (Dissertation, Amsterdam, 1919; compare *Rec. trav. chim.*, 1921, **40**, 1).

Since these two authors arrived at opposite conclusions from the study of the same compound, we thought it desirable to make use of the experience which we had gained in the isolation of the two pure isomerides in order to carry out measurements of solubility under similar conditions to those used by Vixseboxse. For this purpose the purified material was crushed in an agate mortar and stirred vigorously with 5 c.c. of solvent in a vessel mounted in a thermostat; a sufficient quantity of solid was used to make the liquid cloudy, but a little fine powder was added 2 minutes before a sample of the saturated solution was taken for analysis, in order to ensure saturation. The sample was removed by means of a 1 c.c. pipette, with a piece of filter paper wired over the tip; it was transferred to two weighing bottles, evaporated in a current of air, and finally dried for 18 hours over sulphuric acid and paraffin wax in a vacuum desiccator. The time at which samples were taken was fixed at 8 minutes, after a trial run with enolic benzoylcamphor in ethyl alcohol at 15°, which gave the following solubilities :

Time (mins.)	4½	9	13½	30
Conc. (g./100 g. of solution)	3·1	3·1	3·0	3·7

The solubilities found in this way are set out in Table III, where the subscripts A and B relate to enol and ketone, respectively, and the figures shown in parentheses are data cited from Vixseboxse's paper or read off from his graphs.

TABLE III.

Solubility of Benzoylcamphor at 17°.

	Solubility,							
	g. per 100 g. of solution.			mols. per 100 mols. of solution.				
Solvent.	Enol.	Ketone.	Ratio.	$l_{\rm A}$.	$l_{\rm B}$.	$l_{\rm A}/l_{\rm B}$.	$c_{\rm A}/c_{\rm B}$.	G.
Alcohol	3·37	2·95	1·14	0·62	0·54	1·15	1·44	1·25
				(0·71)	(0·58)	(1·22)	(1·56)	(1·28)
Acetone	19·0	19·3	0·98	5·05	5·1	0·99	1·12	1·13
				(5·0)	(5·2)	(0·96)	(1·08)	(1·13)
Benzene	37·3	16·9	2·21	15·3	5·8	2·64	3·55	1·34
Toluene	—	—	—	(12·1)	(4·1)	(2·95)	(4·56)	(1·52)

In the case of acetone our ratios agree throughout with those of Vixseboxse, and give an identical value for the constant $G = 1{\cdot}13(1{\cdot}13)$. In the case of alcohol, our solubilities are slightly lower, but lead to almost the same value for $G = 1{\cdot}25(1{\cdot}28)$. The solubilities in benzene and toluene do not afford any similar check on one another; but they concur in giving a higher value for the constant $G = 1{\cdot}33$*(1·52). The concordance of the values given by Vixseboxse and by ourselves for solutions in acetone and in alcohol shows that the difference in the magnitude of the constant in these two solvents is real; it is also clear that the aromatic hydrocarbons give still higher values. Van 't Hoff's theorem is therefore not an exact relationship; but, since the three values which we have obtained cover a range of only ± 8%, we can at least regard it as a good first approximation.

As a further check on the composition of the equilibrium mixture, we have determined the ratio of the initial and final solubilities of the enol in alcohol, acetone, and benzene. The results are included in Table I, but alcohol is the only solvent in which the solubility is sufficiently low to permit of a trustworthy deduction of the equilibrium ratio from the solubilities. The ratio of the initial to

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* This value would be increased to 1·6 if the solubilities were expressed in g. per 100 g. of solution instead of in mols. per 100 mols.

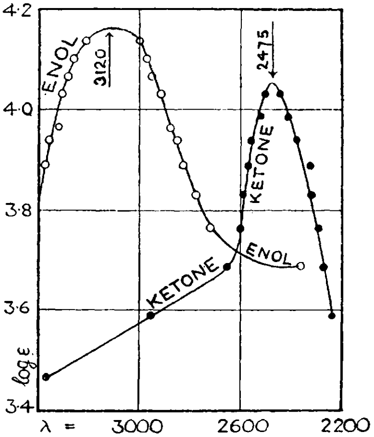
the final solubility (*viz.*, 3·37/5·83) in this solvent indicates that there is 58% of enol in the equilibrium mixture; this proportion agrees closely with the value, 59%, deduced from the optical rotations, and therefore indicates (but does not prove) that only the two known isomerides play any important part in the final equilibrium.

Absorption Spectra.—The first series of absorption spectra were measured with a sector-photometer and a quartz spectrograph (compare Lowry and French, *Proc. Roy. Soc.*, 1924, *A*, **106**, 489), *N*/10,000 alcoholic solutions being used. The absorption curves (Fig. 1) show a very strong enolic band, the molecular extinction coefficient rising to a maximum log ε = 4·19 at 3120 Å.U. The pure ketone, on the other hand, gave a band of its own with a maximum log ε=4·06 at 2475 Å.U. The optical purity of the two specimens is shown by the fact that the molecular extinction coefficient of the enol passes through a *minimum* at a wave-length near to that at which the absorptive power of the ketone rises to a *maximum*, and conversely that the absorptive power of the ketone falls rapidly throughout the region in which that of the enol is rising from a minimum at 2570 to a maximum at 3100 Å.U. The equilibrium mixture of the two forms showed both maxima, the enolic band giving a maximum log ε = 3·95 at 3100 Å.U. and the ketonic band a maximum log ε = 3·80 at 2475 Å.U.

Fig. 1.

Extinction coefficients of benzoyl-camphor.

(*First series: sector-photometer.*)



These observations showed clearly that, in direct opposition to Morton and Rosney's statement, the intensities of the absorption bands of the two forms were approximately equal to one another, whilst the frequencies were quite different; but in order that there should be no possible doubt as to which series of data is correct, the whole of the work was repeated with fresh materials, as part of a more extensive investigation of the physical properties of the two isomerides. In this case an ultra-violet spectro-photometer was used in place of the sector-photometer, since the data given by the latter may be influenced by the characteristic curve of the photographic plate. The results of this second series of measurements are plotted in Fig. 2. The enol now shows a maximum, log ε

= 4·27 at 3140 Å.U., whilst the ketone gives a maximum at log ε = 4·21 at 2420; in the equilibrium mixture, the enolic band gave a maximum at log ε = 4·10 and the ketonic band at log ε = 3·90. No trace of the enolic band was detected in solutions of the pure ketone when the observations were completed in a sufficiently short period of time to avoid the occurrence of isomeric change; but the enolic band was readily observed in specimens which had partly reverted to the enolic form on storage, and it was always seen in solutions which had been kept long enough to allow of a partial isomeric change.* The fact that Morton's specimen of the ketone

Fig. 2.

Extinction coefficients of benzoylcamphor.

(*Second series: spectro-photometer.*)

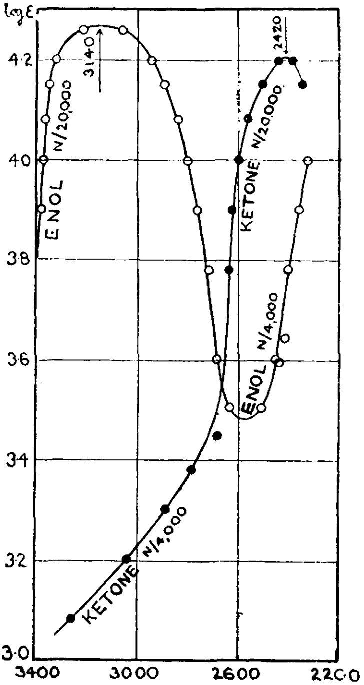
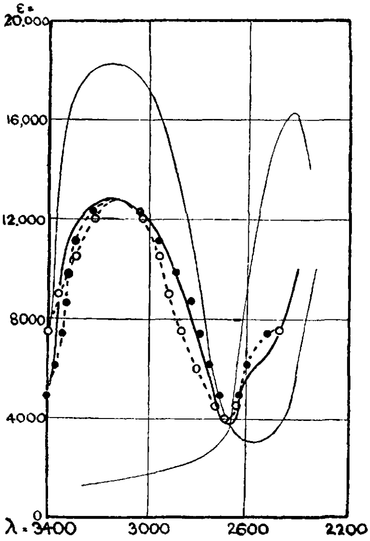


Fig. 3.

Extinction coefficients of equilibrium mixture.

(*Full line = calculated values; broken lines = observed values.*)



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* The enolic band, in a mutarotating solution of the ketone, was first recorded after ½ hour at $\lambda = 2860$, $\log \epsilon = 3{\cdot}36$, and then drifted across slowly to the normal wave-length $\lambda = 3140$ and intensity $\log \epsilon = 4{\cdot}1$ of the band in the equilibrium mixture. It was also noticed that the extinction coefficient for the wave-length $\lambda = 2660$ (at which the values for the ketone, enol, and equilibrium mixture are identical at $\log \epsilon = 3{\cdot}6$) appeared to pass through a minimum value, instead of remaining constant, during the mutarotation of the enolic form.

gave a weak band at the wave-length of the enolic maximum could be explained by supposing that his solution contained some of the more stable enolic isomeride; but it is more surprising that he makes no mention of the band at 2420 Å.U., since this is only slightly less intense than the enolic band itself.*

Although the visual readings of a spectrophotometer plate are not of a high order of accuracy, the fact that they give numerical values for the molecular extinction coefficient of the solute makes it possible to use them as the basis of an independent determination of the proportions of enol and ketone in the equilibrium mixture. Thus, if we select for examination the extinction coefficients at wave-lengths corresponding with the enolic and ketonic maxima respectively, we obtain the following results :

	Molecular extinction coefficients.			Equilibrium ratio.	
Wave-length.	Enol.	Ketone.	Equilibrium mixture.	Enol.	Ketone.
$\lambda = 3140$	18,400	1,300	12,600	66	34
$\lambda = 2420$	4,300	16,200	8,000	69	31

The equilibrium ratio deduced by Dimroth and by Vixseboxse from bromine titrations was 61 : 39 for saturated solutions in alcohol, and this agrees closely with the ratios 60 : 40 and 59 : 41 deduced by Vixseboxse and by ourselves from observations of optical rotatory power. The ratios deduced from the absorption spectra for alcoholic solutions of about $M/20{,}000$ concentration show a higher percentage of enol, but, since they agree very well with one another, this higher ratio may be regarded as a definite change of equilibrium resulting from the extreme dilution of the solution.

Summary.

(*a*) Measurements have been made of the melting point, optical rotation, rotatory dispersion, solubility, and ultra-violet absorption of the stable and labile forms of benzoylcamphor.

(*b*) Contrary to an earlier statement "that the two isomeric forms of benzoylcamphor give bands at the same wave-length, but of unequal intensity," it has been found that the absorption bands are of nearly the same intensity, but differ widely in wave-length. The absorption of the equilibrium mixture in very dilute alcoholic solutions corresponds closely with that of a mixture of two parts of enol and one part of ketone.

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* [Note added, *May* 11*th*, 1928.] Dr. Morton has been kind enough to prepare fresh samples of the two isomerides from a specimen of crude benzoylcamphor which we sent to him, and has confirmed the general form of the absorption spectra recorded in Fig. 2. The origin of the different results recorded previously is under investigation.

(*c*) Van 't Hoff's relation between the solubilities of the two forms and their equilibrium concentrations has been tested for solutions in alcohol, acetone, and benzene, and found to hold good within ± 8%.

(*d*) The ratio of the initial and final solubilities of the enolic form indicates that the equilibrium mixture in a saturated alcoholic solution contains about 58% of enol, in close agreement with the proportion, 59%, deduced from the optical rotations of the solutions.

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