475. *The Stereochemistry of* 10-*Benzylideneanthrone and* 9-*Benzylidenefluorene.*

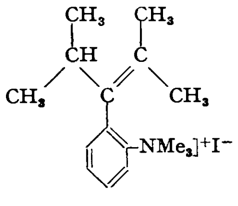
By V. M. INGRAM.

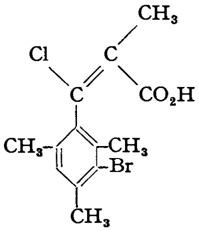
10-*m*-Aminobenzylideneanthrone was expected to show restricted rotation about the single bond between the phenyl group and its side-chain, but it could not be resolved by recrystallisation of its (+)-camphor-10-sulphonate. Optical activity was established by the mutarotation of this salt and by the preparation of an active hydriodide. The *N*-(—)-menthoxyacetyl derivative of the base also resisted resolution, but gave indications of optical activity in its basic portion.

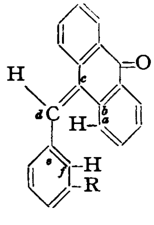
9-*m*-Aminobenzylidenefluorene dibenzoyl-D-tartrate could not be resolved, neither did it mutarotate, but comparison with similar salts of inactive bases gave an indication that the base might be capable of optical activity. The *N*-(—)-menthoxyacetyl derivative proved to be inactive.

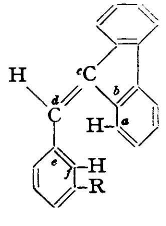
MILLS and DAZELEY (*J.*, 1939, 460) and Adams and Miller (*J. Amer. Chem. Soc.*, 1940, **62**, 53) were able to show that arylolefins of the types (I) and (II) exhibited restricted rotation about the single bond joining the phenyl nucleus to the side-chain. In order to ensure sufficient restriction, these compounds possessed either one very large *ortho*-substituent or two smaller ones. The present work was undertaken with the object of increasing the size of the side-chain to such an extent, as in 10-benzylideneanthrone derivatives (III), that there would be restricted rotation with only hydrogen atoms in the *ortho*-positions.

A scale drawing of the essential (lettered) part of (III), constructed by using the usual interatomic distances and valency angles, indicated that, although carbon atoms *a* and *f* do not interfere, the centres of the hydrogen atoms attached to them overlap by approximately 0·2 A. As a result the benzene ring can no longer lie in the same plane as the 10-methylene-anthrone skeleton, which is itself rigidly planar, and rotation around the single bond C(*d*)—C(*e*) will be effectively restricted. Unsymmetrical substitution in the benzene ring, as in 10-*m*-aminobenzylideneanthrone (III; R = NH_2), will then give rise to an asymmetric molecule which should exist in two optically-active forms.


(I.)


(II.)


(III.)


(IV.)

10-*m*-Aminobenzylideneanthrone was readily prepared by the reduction of the corresponding nitro-compound with stannous chloride in glacial acetic acid saturated with hydrogen chloride. Attempts to resolve this base by crystallisation of the (+)-camphor-10-sulphonate from alcohol were unsuccessful, as successive crops had identical rotations in pure chloroform, $[M]^{20}_{\mathrm{D}} = +98°$, $+98°$. No further attempts at fractionation were made especially as it was found that the base was too weak to form stable salts with optically-active carboxylic acids. The solution of the salt in pure chloroform showed no change in rotation during 10 hours. Addition of alcohol (3·25%) to the chloroform solution produced, however, a change in the value of rotation, and mutarotation which was measured at three temperatures, *viz*. 20·0°, 30·0°, and 35·0° (see Table I and Fig. 1). It is evident that the reaction obeyed a first-order law. From the results it was calculated that the half-life periods were 302, 185, and 127 minutes, respectively, whilst the activation energy for the mutarotation was 10·1 kcals./mol.

This value is one of the lowest recorded for the mutarotation of compounds showing restricted rotation. It is of interest since, according to Kistiakowsky and Smith (*J. Amer. Chem. Soc.*, 1936, **58**, 1043), 20 kcals./mol. is the minimum value required before isolation of the optical isomers can be expected.

TABLE I.

	Salt.	Treatment.	Temp.	$[M_0]_{\mathrm{D}}$.	$[M_\infty]_{\mathrm{D}}$.	10^4k ($\mathrm{min.}^{-1}$).	Half-life period, mins.	Remarks.
(1)	10-*m*-Aminobenzylidene-anthrone (+)-camphor-10-sulphonate	cryst.	20·0°	+ 98°	—	—	—	*c*, 2·667; no mutarotation
(2)	,, ,,	,,	20·0	+135°	+72°	23	302	energy of activation = 10·1 kcals.
(3)	,, ,,	,,	30·0	+133	+50	38	185	
(4)	,, ,,	,,	35·0	+132	+44	55	127	
(5)	,, ,,	synthesised in soln.	30·0	+125	+50	32	219	different batch of solvent
(6)	,, ,,	synthesised in soln.; boiled	30·0	− 55	+50	32	219	
(7)	Pyridine (+)-camphor-10-sulphonate	synthesised in soln.	30·0	+128	—	—	—	
(8)	10-*m*-Aminobenzylidene-anthrone hydriodide	see text	20·0	−187	0	12	600	

Solvents: pure chloroform in (1), pure chloroform containing 3·25% of alcohol (added immediately before the observations were commenced) in all others.

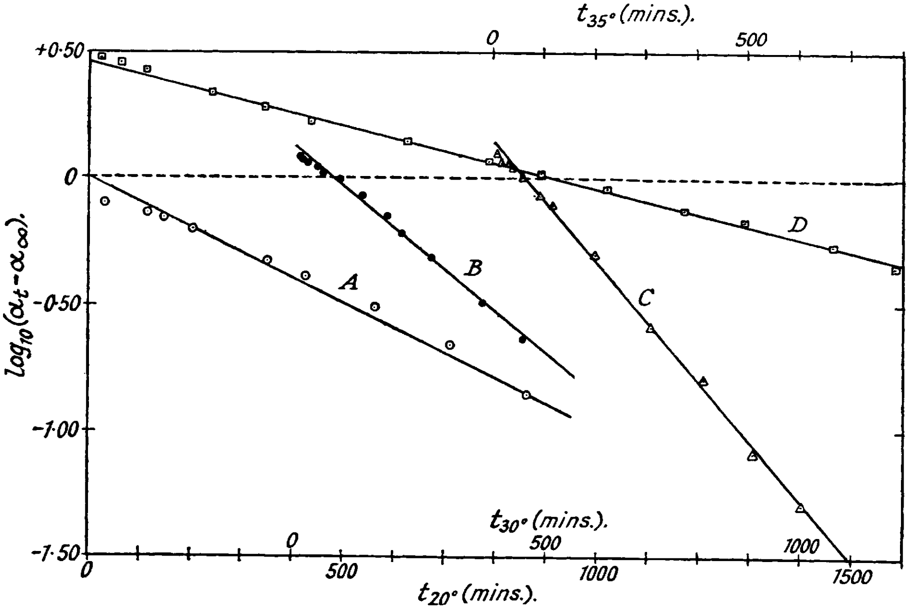
Concentration: *c*, 4·164 in (2)—(6); equimolecular concentrations in (7) and (8).

From the experimental results recorded in Table I it will be noticed that the initial rotation of 10-*m*-aminobenzylideneanthrone (+)-camphor-10-sulphonate at 30° $[M_0]^{30}_{\mathrm{D}} = +133°$, lies remarkably close to the rotation of pyridine (+)-camphor-10-sulphonate in the same solvent, $[M]^{30}_{\mathrm{D}} = +128°$, the difference between these two values being very small compared with the change in rotation which occurs during the mutarotation, $[M]^{30}_{\mathrm{D}} = +133° \longrightarrow +50°$. The conclusion was therefore drawn that the basic portion of the molecule makes no contribution to the initial rotation and that the crystalline salt consists of a mixture, or perhaps a compound, of the two salts (+)-base(+)-acid and (−)-base(+)-acid, in molecular proportions.

A solution prepared from equimolecular amounts of the (±)-base and (+)-camphor-10-sulphonic acid in chloroform containing alcohol (3·25%) had an initial rotation of $[M_0]_{\mathrm{D}}^{30} = +125^\circ$ and then mutarotated to the same equilibrium value $[M_\infty]_{\mathrm{D}}^{30} = +50^\circ$, as that found for the crystallised salt (see Table I and Fig. 2). The initial value is very close to that of the original crystallised salt, which therefore contains equal amounts of the (+)- and (−)-bases.

The mutarotation of the "synthetic" salt proceeded at a slower rate than that of the original crystallised salt, the half-life period being 219 minutes as compared with 185 minutes, but this lower speed is probably due to the fact that different specimens of chloroform were employed in the two experiments. It had been found previously that the rate of mutarotation was dependent on the manner in which the solvent had been purified.

FIG. 1.



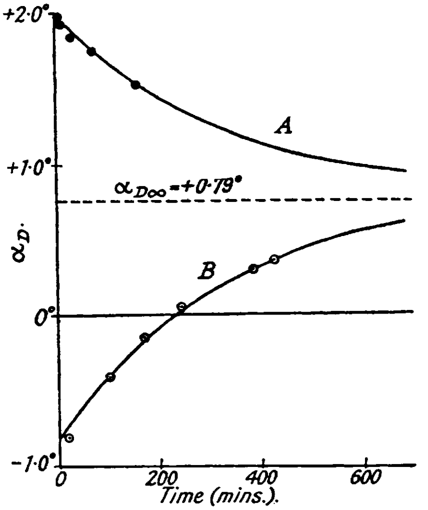
A ⎫   ⎧ *at* 20°.
B ⎬ (±)-10-m-*Aminobenzylideneanthrone* (+)-*camphor*-10-*sulphonate* ⎨ *at* 30°.
C ⎭   ⎩ *at* 35°.
D *Activated* 10-m-*aminobenzylideneanthrone hydriodide.*

From the values of $[M_\infty]_{\mathrm{D}}$ at 20° and 35° given in Table I it will be observed that the positive rotation of the equilibrium mixture diminishes rapidly with rise of temperature, indicating a displacement of the equilibrium in favour of the salt derived from the (−)-base. At the temperature of boiling chloroform the displacement occurs to such an extent that the equilibrium mixture shows actually a negative rotation. Thus a chloroform solution of the "synthetic" salt, prepared as described previously, after being heated to boiling and rapidly cooled to 30° had an initial rotation of $[M_0]_{\mathrm{D}}^{30} = -55^\circ$ which changed at the same rate as before to the same final value (see Table I and Fig. 2). Since there is no reason to suppose that −55° represents the maximum rotation of the optically pure (−)-base(+)-acid salt, the base must have a molecular rotation greater than ±180°.

Final confirmation of the optical activity of 10-*m*-aminobenzylideneanthrone was obtained by the preparation of a lævorotatory hydriodide. A solution of the "synthetic" (+)-camphor-10-sulphonate in chloroform containing 3·25% alcohol was heated to boiling, cooled rapidly to 20°, and then vigorously shaken with concentrated aqueous potassium iodide. The hydriodide remaining in the chloroform solution had an initial rotation of −187°, and then underwent mutarotation with a half-life period of 600 minutes, obeying a first-order law (see Fig. 1). The progressive darkening of the solution prevented direct observation of the final zero reading, but the actual observations agreed very well with the values calculated by the method of least squares on the assumption of a final zero reading.

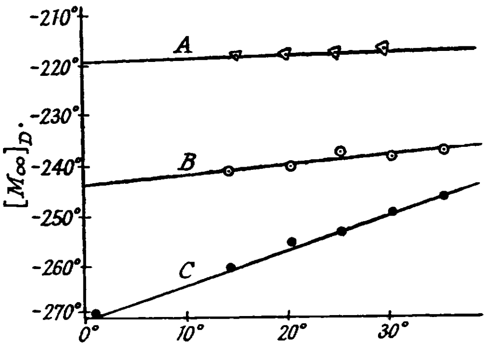
10-*m*-[(—)-Menthoxyacetamido]benzylideneanthrone, prepared from (—)-menthoxyacetyl chloride, could not be resolved by crystallisation from alcohol and ethyl acetate, the first and the second crop having almost identical rotations, *viz.* $[M]_D^{20} = -255°$ and $-254°$ in chloroform, respectively. The rotations remained constant during 2½ hours and showed no change even after the addition of alcohol, glacial acetic acid, or alcoholic hydrogen chloride to the chloroform solution; heating in methyl salicylate to 150° for one hour also produced no change. On the other hand the rotation in chloroform solution showed a marked increase with rise of temperature compared with that of (—)-menthoxyacetanilide (see Fig. 3). This increase may of course be the ordinary variation of rotatory power with temperature, but it could also be connected with the existence of the benzylideneanthrone part of the molecule in optically active forms. The two diastereoisomeric menthoxyacetyl derivatives [(—)-acyl(—)amine and (—)-acyl(+)-amine)] may racemise too rapidly to permit of the mutarotation being followed by direct polarimetric observation, but would form equilibrium mixtures of varying composition at different temperatures; this variation in composition may manifest itself by a marked change in the equilibrium values of the rotation with rise of temperature.

FIG. 2.



A "*Synthetic*" 10-m-*aminobenzylideneanthrone* (+)-*camphor*-10-*sulphonate.*
B *Boiled* 10-m-*aminobenzylideneanthrone* (+)-*camphor*-10-*sulphonate.*

FIG. 3.



A 9-m-[(—)-*Menthoxyacetamido*]*benzylidenefluorene.*
B (—)-*Menthoxyacetanilide.*
C 10-m-[(—)-*Menthoxyacetamido*]*benzylideneanthrone.*

The carbon skeleton *a*—*f* in 9-benzylidenefluorene (IV; R = H) is very similar to that present in 10-benzylideneanthrone, but the replacement of the 6-membered *centre* anthrone ring by a 5-membered ring in fluorene must result in a considerable increase in the distance between carbon atoms *a* and *f*. Nevertheless it was expected that restricted rotation would occur, though the optical stability of the molecule should be less than in the case of its anthrone analogue.

9-*m*-Nitrobenzylidenefluorene (IV; R = NO_2) was prepared by a method similar to that used by Thiele and Henle (*Annalen*, 1906, **347**, 296) for the preparation of 9-benzylidenefluorene. Reduction with stannous chloride in ether saturated with hydrogen chloride furnished the amine hydrochloride (IV; R = NH_2,HCl). The free base could not be obtained crystalline. The (+)-camphor-10-sulphonate of this base was unsuitable for optical examination because of its very sparing solubility in neutral organic solvents. The more soluble dibenzoyl-D-tartrate could not be resolved by crystallisation from alcohol, successive fractions having almost identical rotations $[M]_D^{20} = -353°$, $-349°$. As there was also no evidence of mutarotation, the molecular rotation of this salt was compared, under identical conditions, with the rotations of dibenzoyl-D-tartrates of the inactive bases, pyridine, 1-naphthylamine, and 9-*m*-aminobenzylfluorene (see Table II). The rotation given in (4) refers to the crystallised salt of the fluorene base, whilst the values in (5) and (6) were obtained from solutions of the salt prepared directly from the base and the acid immediately before optical examination.

TABLE II.

Base.	Molar ratio, base : acid.	$[M]_D^{20}$.
(1) Pyridine	2 : 1	−420°
(2) 1-Naphthylamine	2 : 1	−417
(3) 9-*m*-Aminobenzylfluorene	2 : 1	−418
(4) 9-*m*-Aminobenzylidenefluorene (cryst. salt)	2 : 1	−354
(5) ,, ,, (synth. salt)	2 : 1	−345
(6) ,, ,, ,,	4 : 1	−259

Solvent : pure chloroform containing 3·25% of alcohol. *c*, 0·726 in (4), corresponding molarities in the others.

It will be observed that whereas the rotations of the salts of the inactive bases lie within ±2°, or 0·5% of their mean value −419°, the rotation of 9-*m*-aminobenzylidenefluorene dibenzoyl-D-tartrate differs by as much as 65°, or 15%. This difference would appear to indicate that there is a contribution by the base to the total rotatory power of the salt, a conclusion which implies that 9-*m*-aminobenzylidenefluorene might be capable of existing in optically-active modifications and that the salt, at any rate in solution, may contain a preponderance of the dextrorotatory form. Since the rotation of the dibenzoyl-D tartrate, "synthesised" in solution from the acid and the free (±)-base [Table II (5)], is very near in value to that of the crystallised salt (4), it follows that the base present in the salt undergoes mutarotation to form an equilibrium mixture containing an excess of the dextrorotatory form, the rate of racemisation being too rapid for visual observation.

Further support for these conclusions is afforded by the marked effect which the addition of an excess of free (±)-base exercise on the rotation of the "synthetic" salt [Table II (6)]; no significant change would be expected, if the base is incapable of existing in optically-active forms. The small difference in rotation of the crystallised and "synthetic" salts recorded in (4) and (5) can be readily understood when it is remembered that the base employed in the preparation of the solution of the "synthetic" salt could not be crystallised; in order to ensure that the neutralisation of the acid was complete a slight excess of the base was employed.

9-*m*-[(−)-Menthoxyacetamido]benzylidenefluorene could not be resolved by crystallisation. It showed no observable mutarotation and only very slight variation of rotation with temperature (see Fig. 3).

EXPERIMENTAL.

M. p.s and b. p.s are uncorrected. Most of the microanalyses are by Drs. Weiler and Strauss of Oxford.

10-m-*Nitrobenzylideneanthrone*.—This compound was prepared by boiling a mixture of anthrone (90 g.), *m*-nitrobenzaldehyde (75 g.), piperidine (7 c.c.), pyridine (80 c.c.), and xylene (190 c.c.) in an atmosphere of coal gas for 6 hours. The product (82 g., 55%) which separated from the cool solution was washed with cold acetone and then with the same solvent containing a little hydrochloric acid, and finally crystallised from acetic acid; it formed small canary-yellow prisms which exhibited pronounced thermochromism and had m. p. 174·5—175·5° (Found : C, 77·3; H, 4·0; N, 4·2. Calc. for $C_{21}H_{13}O_3N$: C, 77·1; H, 4·0; N, 4·3%). Padova (*Ann. Chim. Phys.*, 1910 (8), **19**, 386; *Compt. rend.*, 1905, **141**, 861) gives m. p. 165·5—166·5°.

10-m-*Aminobenzylideneanthrone*.—Dry hydrogen chloride was passed into a suspension of powdered, fused stannous chloride (105 g.) in glacial acetic acid (550 c.c.) until solution was effected. On the addition of 10-*m*-nitrobenzylideneanthrone (50 g.), dissolved in boiling acetic acid (450 c.c.), 10-*m*-aminobenzylideneanthrone stannichloride was rapidly deposited in slender, crimson needles which after being successively washed with acetic acid and alcohol, were suspended in the latter solvent (500 c.c.) and warmed with aqueous ammonia (70 c.c.; 0·88). The solid was separated, digested with cold aqueous sodium hydroxide (300 c.c.; 4N.) in order to remove stannic hydroxide, washed with water, and combined with the product obtained by precipitating the alcoholic mother-liquor with water. The solids were dried azeotropically in toluene solution (200 c.c.) by using a Dean and Stark water separator. The hot solution was decanted from the residual tin compounds and ammonium chloride which were again extracted with toluene (50 c.c.). The combined toluene extracts, after clarification with charcoal, deposited 10-m-*aminobenzylideneanthrone* in soft yellow needles (30 g., 66%) which had m. p. 172—173° (sintering at 157°) and showed no signs of thermochromism (Found : C, 84·2; H, 5·0; N, 4·6. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·1; N, 4·7%).

The (+)-*camphor*-10-*sulphonate* was prepared from equivalent quantities of the base (6·0 g.) and the acid (4·6 g.) in boiling alcohol (120 c.c.), and separated in rosettes of soft yellow needles (7·0 g.), m. p. 190·5—192·5°, $[M]_D^{20}$ +98° in pure chloroform ($\alpha_D^{20} = +0·99°$, $l = 2$, $c = 2·667$) (Found: C, 69·8; H, 5·9; N, 2·6. $C_{31}H_{31}O_5NS$ requires C, 70·3; H, 5·9; N, 2·6%). The mother-liquor furnished a second crop of the salt (0·9 g.) having the same rotatory power in pure chloroform, $[M]_D^{20} = +98°$ ($\alpha_D^{20} = +0·78°$, $l = 2$, $c = 2·105$). Neither of the crops showed any change in rotation during 10 hours.

Mutarotation of (±)-10-m-*Aminobenzylideneanthrone* (+)*Camphor*-10-*sulphonate*.—The chloroform employed in the following experiments was purified by freeing it from alcohol by prolonged washing with running water, followed by azeotropic drying. The dry chloroform was finally fractionally distilled through a 2-ft. column packed with glass helices; it usually boiled over a range of ±0·1°, and did not develop any acidity when kept in the dark for several months.

All polarimetric determinations were made in jacketed 2-dm. tubes maintained within ±0·1° of the stated temperature; the sodium-D line was used. Solutions in chloroform–alcohol were prepared by dissolving the compound for examination in chloroform and adding the absolute alcohol immediately before commencing the observations. The solutions were made up at the same temperature as that at which the determinations were carried out.

The values of k and the half-life period (see Table I) were determined from the best straight line (see Fig. 1) calculated by the method of least squares from the plot of $\log_{10} (\alpha_t - \alpha_\infty)$ against the time, t. From the values of k obtained at the three temperatures the energy of activation for the mutarotation of (±)-10-*m*-aminobenzylideneanthrone (+)-camphor-10-sulphonate in chloroform containing 3·25% of alcohol was found to be 10·1 kcals./mol.

Rotation of Pyridine (+)-*Camphor*-10-*sulphonate*.—A solution of this salt was examined at 30·0° under the same conditions and at the same molar concentration as in the previous experiments; it showed no change in rotation during 12 hours.

Mutarotation of " Synthetic " (±)-10-m-*Aminobenzylideneanthrone* (±)-*Camphor*-10-*sulphonate*.—The solution became too dark for further observation after 154 minutes.

A second solution of the same " synthetic " salt, having the same concentration, was heated under reflux on the steam-bath for 2 hours, cooled rapidly to 30°, and then examined polarimetrically at the same temperature. The solution became too dark for readings to be taken after 425 minutes.

Note : The sample of chloroform used in these and the following experiment was from a different batch from that previously employed. Although both batches had apparently had the same treatment in purification, it had been noticed that the rate of mutarotation is extremely sensitive to minute traces of impurities, and it has been impossible to obtain two batches of chloroform with the same characteristics.

Optically-active 10-m-*Aminobenzylideneanthrone Hydriodide*.—A solution of " synthetic " (±)base-(+)-camphor-10-sulphonate in chloroform containing 3·25% of alcohol was boiled under reflux for 2 hours, then rapidly cooled to 15° and shaken vigorously for two minutes with an aqueous solution of potassium iodide (20 g. in 20 c.c.). The chloroform solution was separated, filtered, and then examined polarimetrically at 20·0°. For the calculation the time at which the shaking with potassium iodide commenced was taken as the zero time of the mutarotation. The solution became too dark after 1585 minutes.

10-m-[(—)-*Menthoxyacetamido*]*benzylideneanthrone*.—A solution of (—)-menthoxyacetyl chloride (11·5 g.) in anhydrous ether (50 c.c.) was added slowly during 20 minutes to a boiling suspension of 10-*m*-aminobenzylideneanthrone (15·0 g.) in the same solvent (50 c.c.) containing slightly more than the equivalent amount of pyridine (5 c.c.). The mixture was then heated under reflux for 1½ hours, the solid being occasionally broken up during this period. The precipitated pyridine hydrochloride was removed from the cold reaction mixture and washed several times with ether. The ethereal solution was washed successively with dilute hydrochloric acid and water and furnished 10-m-[(—)-*menthoxyacetamido*]*benzylideneanthrone* in pale-yellow needles (22·5 g., 90%), which crystallised from ethyl acetate and had m. p. 124·5° and $[M]_D^{20} = -255°$ in chloroform ($\alpha_D^{20} = -7·04°$, $l = 2$, $c = 6·81$) (Found : C, 80·2; H, 7·2. $C_{33}H_{35}O_3N$ requires C, 80·3; H, 7·2%).

Concentration of the ethyl acetate mother-liquor yielded a second crop (1·5 g.), m. p. 123—124°, $[M]_D^{20} = -254°$ in chloroform ($\alpha_D^{20} = -7·06°$, $l = 2$, $c = 6·84$).

In chloroform containing 1% of alcohol the observed rotation, $[M]_D^{20} = -242°$, did not change during 6 hours. On the addition of 0·1 c.c. of a 4% alcoholic solution of concentrated hydrochloric acid to the chloroform solution (20·2 c.c.) there was no significant change during 15 hours. In chloroform containing 3·25% of alcohol the molecular rotation of −240° at 30° remained constant over 24 hours and also after addition of 0·1 c.c. of glacial acetic acid to the solution (20·65 c.c.). In methyl salicylate it gave $[M]_D^{30} = -291°$, and this value remained constant when the solution was heated for one hour at 100° and later for one hour at 150°.

Comparison of the Rotations of 10-m-[(—)-*Menthoxyacetamido*]*benzylideneanthrone and* (—)-*Menthoxyacetanilide*.—A solution of the benzylideneanthrone derivative in chloroform ($c = 6·84$ at 14°) was examined at temperatures between 14° and 35°; its rotation was also measured at 1°.

A solution of (—)-menthoxyacetanilide of the same molar concentration was examined under the same conditions. This solution was prepared by adding freshly distilled aniline (1·301 g., 2 mols.) to (—)-menthoxyacetyl chloride (1·613 g.) dissolved in chloroform. A white crystalline precipitate of aniline hydrochloride separated immediately and the reaction was completed by gentle boiling for one hour. The mixture was cooled and made up to 50·0 c.c. with chloroform and before examination was strained through cotton wool. The results are given in Fig. 3; the expansion of the solution has been taken into account.

9-m-*Nitrobenzylidenefluorene*.—Warm alcoholic solutions of sodium (30 g. in 500 c.c.) and *m*-nitrobenzaldehyde (130 g. in 300 c.c.) in absolute alcohol were added successively to a hot solution of technical fluorene (100 g.) in the same solvent (2 l.). The solution became very dark and, when kept overnight, deposited a brown crystalline solid which, after being washed with alcohol and then with dilute hydrochloric acid, was dissolved in ethyl acetate (600 c.c.) and allowed to percolate through a

12-in. column of activated alumina. Concentration of the red percolate to 200 c.c. furnished 9-m-*nitrobenzylidenefluorene* (44 g., 24·5%) which, after crystallisation from alcohol containing ethyl acetate (10%), had m. p. 115—115·5° and showed no signs of thermochromism (Found : C, 80·2; H, 4·5; N, 4·7. $C_{20}H_{13}O_2N$ requires C, 80·3; H, 4·4; N, 4·7%).

9-m-*Aminobenzylidenefluorene*.—Dry hydrogen chloride was passed into a well-stirred suspension of finely powdered, fused stannous chloride (100 g.) in anhydrous ether (1250 c.c.) until the solid had disappeared and a lower viscid layer had separated out. After the portionwise addition of 9-*m*-nitrobenzylidenefluorene (44 g.) the mixture was stirred for a further 5 hours whereupon 9-*m*-aminobenzylidenefluorene stannichloride separated as a buff-coloured solid in theoretical yield (68 g.). A solution of the stannichloride in hot alcohol (200 c.c.) deposited, on cooling, very pale-yellow needles of 9-m-*aminobenzylidenefluorene hydrochloride* (22 g., 49%) which after further crystallisation from alcohol had m. p. 229—230°. A second crop (18·5 g.; total yield 90%) of the hydrochloride was obtained by adding aqueous ammonia (80 c.c.; *d* 0·88) to the alcoholic mother-liquor, filtering from the stannic hydroxide thus precipitated, and pouring into dilute hydrochloric acid (4 l.; 2N.) (Found : C, 78·3; H, 5·6; N, 4·3. $C_{20}H_{16}NCl$ requires C, 78·6; H, 5·3; N, 4·6%. Found : 1·00 g. neutralised 32·2 c.c. of 0·1N-sodium hydroxide. 1·00 g. of $C_{20}H_{15}N,HCl$ requires 32·7 c.c. of 0·1N-sodium hydroxide).

The free base was obtained as an amorphous yellow solid by stirring the finely powdered hydrochloride (1·0 g.) with dilute aqueous ammonia (5 c.c. of *d* 0·88 solution in 200 c.c. of water). All attempts to obtain the base crystalline were unsuccessful. It decomposes when kept, and was therefore always freshly prepared.

9-m-*Aminobenzylidenefluorene* (+)-*Camphor*-10-*sulphonate*.—This salt was prepared by heating the hydrochloride (9·67 g.) and silver (+)-camphor-10-sulphonate (10·68 g.) in boiling absolute alcohol (400 c.c.). After one hour the solution still contained a slight amount of silver, which was removed by heating it for a further 15 minutes with a few crystals of the amine hydrochloride. The solution was filtered from silver chloride and when cooled deposited the (+)-*camphor*-10-*sulphonate* in pale-yellow needles (11·0 g.) which had m. p. 214—215° and were readily soluble in pyridine and quinoline, but only very sparingly soluble in neutral organic solvents [Found : C, 71·8; H, 6·4; N, 2·8%; *M* (Rast), 415. $C_{30}H_{31}O_4NS$ requires C, 70·2; H, 6·2; N, 2·8%; *M*, 501]. The salt had $[M]_{\mathrm{D}}^{20} = +80°$ in quinoline ($\alpha_{\mathrm{D}}^{20} = +1·60°$, $l = 2$, $c = 5·00$) and $[M]_{\mathrm{D}}^{20} = +124°$ in chloroform containing 9% by volume of pyridine ($\alpha_{\mathrm{D}}^{20} = +4·46°$, $l = 2$, $c = 9·09$); neither solution showed mutarotation.

9-m-*Aminobenzylidenefluorene Dibenzoyl*-D-*tartrate*.—A solution of the base (5·0 g., 0·02 mol.) and the acid (4·2 g., 0·01 mol.) (containing 1·5 mols. of water of crystallisation) in the minimum amount of boiling alcohol (25 c.c.) deposited, on cooling, the *dibenzoyl*-D-*tartrate* in microscopic, pale-orange needles, m. p. 140°, $[M]_{\mathrm{D}}^{20} = -354°$ in chloroform containing 3·25% of alcohol ($\alpha_{\mathrm{D}}^{20} = -1·15°$, $l = 4$, $c = 0·66$) (Found : C, 77·4; H, 5·0. $C_{58}H_{44}O_8N_2$ requires C, 77·7; H, 5·0%). Concentration of the original mother-liquor furnished a further crop having almost the same rotation, $[M]_{\mathrm{D}}^{20} = -349°$ in chloroform containing 3·25% alcohol ($\alpha_{\mathrm{D}}^{20} = -0·39°$, $l = 2$, $c = 0·50$).

Comparison of Rotations of Several Dibenzoyl-D-*tartrates*.—The rotations of the dibenzoyl-D-tartrates of 1-naphthylamine, pyridine, and 9-*m*-aminobenzylfluorene were compared with the rotations of crystallised and "synthetic" 9-*m*-aminobenzylidenefluorene dibenzoyl-D-tartrate (see Table II). In all cases the solutions were prepared by suspending the salt, or the equivalent quantities of the base and acid, in chloroform (40·0 c.c.) and adding absolute alcohol (1·3 c.c.). The concentration of dibenzoyl-D-tartaric acid was the same in all cases and corresponded to 0·29 g. of the anhydrous acid in 100 c.c. of solution.

9-m-[(−)-*Menthoxyacetamido*]*benzylidenefluorene*.—A suspension of 9-*m*-aminobenzylidenefluorene hydrochloride (15·5 g.) in anhydrous ether (50 c.c.), containing pyridine (10 c.c.), was heated to boiling for ½ hour and a solution of (−)-menthoxyacetyl chloride (11·5 g.) in ether (50 c.c.) was then slowly added. After being heated for a further 2½ hours, the ethereal solution was filtered and washed successively with dilute hydrochloric acid, water, aqueous sodium hydroxide, and water again; it was then dried (Na_2SO_4), and the solvent was removed. The residual syrup could not be crystallised, but after exposure to the laboratory atmosphere for several months it partially solidified. Trituration with light petroleum (b. p. 40—60°) containing a little ether furnished 6·0 g. of 9-m-[(−)-*menthoxyacetamido*]-*benzylidenefluorene*, which on crystallisation from the same solvent separated as a tangled mass of long, slender needles, m. p. 79—80°, $[M]_{\mathrm{D}}^{30} = -220°$ in chloroform ($\alpha_{\mathrm{D}}^{30} = -4·19°$, $l = 2$, $c = 4·48$); there was no evidence of mutarotation. The rotations at different temperatures, in pure chloroform, are recorded in Fig. 3; the values given have been corrected for the expansion of the solution.

Addition of light petroleum (b. p. 40—60°) to the mother-liquor furnished a second crop of the (−)-menthoxyacetyl derivative having m. p. 80—82° and $[M]_{\mathrm{D}}^{30} = -217°$ in chloroform ($\alpha_{\mathrm{D}}^{30} = -4·13°$, $l = 2$, $c = 4·48$) (Found : C, 81·9; H, 7·9. $C_{32}H_{35}O_2N$ requires C, 82·5; H, 7·6%).

9-m-*Aminobenzylfluorene*.—9-*m*-Nitrobenzylidenefluorene (2·0 g.) dissolved in ethyl acetate (75 c.c.) was stirred vigorously in hydrogen at atmospheric pressure with palladised charcoal (0·5 g.; 14%). The reduction, at 42°, was complete in 3 hours. After filtration from the catalyst, the solution was evaporated and furnished 9-m-*aminobenzylfluorene* as a pale-yellow oil which slowly solidified (1·8 g., 99%), and then crystallised from alcohol (15 c.c.) in short cream-coloured prisms, m. p. 105·5—106·5° (Found : C, 87·6; H, 6·4; N, 5·5. $C_{20}H_{17}N$ requires C, 88·5; H, 6·3; N, 5·2%).

BIRKBECK COLLEGE, LONDON, E.C.4.

[*Received, April* 29*th*, 1950.]
