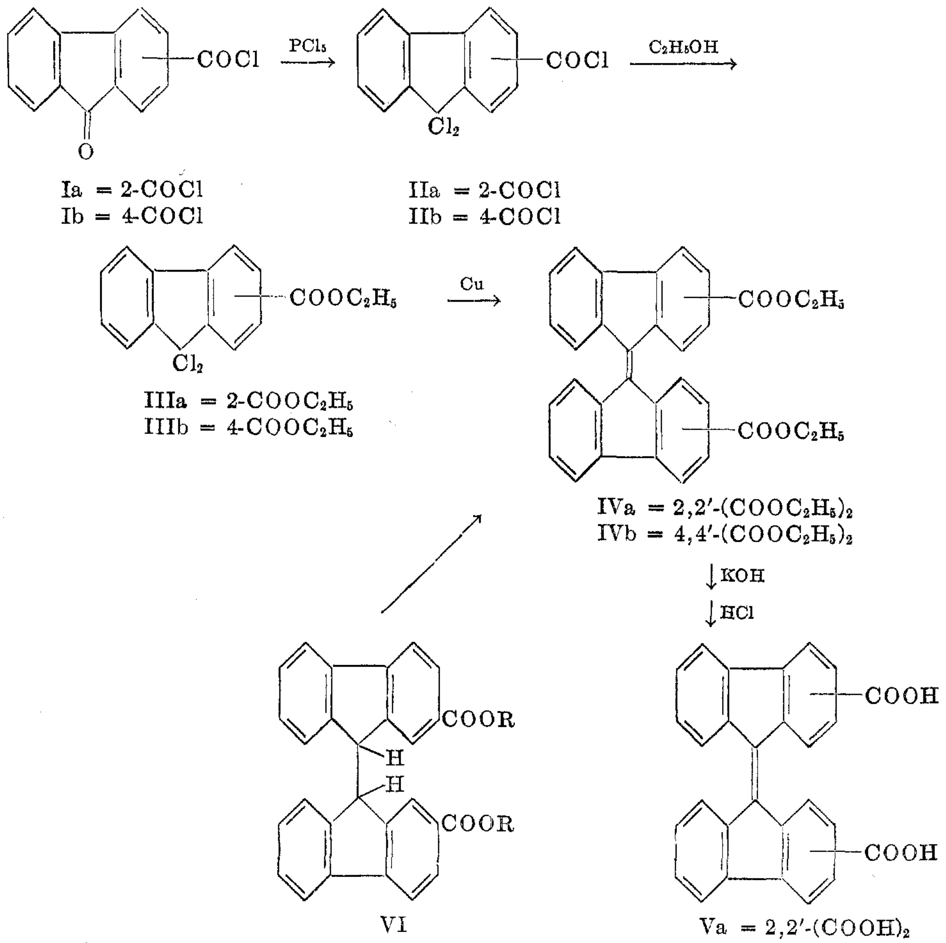
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

STUDIES ON THE POSSIBILITY OF RESOLVING DICARBOXY-$\Delta^{9,9'}$-BIFLUORENES

STANLEY WAWZONEK AND JOSEPH P. HENRY[1]

Received May 21, 1953

Dipole measurements of 2,2′-difluoro-$\Delta^{9,9'}$-bifluorene (1), the polarographic behavior (2) and x-ray crystal structure determination (3) of $\Delta^{9,9'}$-bifluorene and molecular orbital calculations for this compound (4) have indicated that the two fluorene rings in $\Delta^{9,9'}$-bifluorene are non-planar. Such a structure if present should make disubstituted $\Delta^{9,9'}$-bifluorenes similar to optically active biphenyls and hence capable of resolution.



Ia = 2-COCl
Ib = 4-COCl

IIa = 2-COCl
IIb = 4-COCl

IIIa = 2-COOC$_2$H$_5$
IIIb = 4-COOC$_2$H$_5$

IVa = 2,2′-(COOC$_2$H$_5$)$_2$
IVb = 4,4′-(COOC$_2$H$_5$)$_2$

VI

Va = 2,2′-(COOH)$_2$
Vb = 4,4′-(COOH)$_2$

---

[1] Abstracted in part from the Ph.D. thesis of J. P. Henry, August, 1950.

To test this hypothesis 2,2′-dicarboxy-$\Delta^{9,9'}$-bifluorene (Va) and 4,4′-dicarboxy-$\Delta^{9,9'}$-bifluorene (Vb) have been synthesized by the steps shown for the purpose of studying their resolution.[2]

The structures of the esters (IVa, IVb) formed by coupling and the acid (Vb) were demonstrated by atmospheric oxidation to 2-carbethoxy-, 4-carbethoxy-, and 4-carboxy-fluorenone respectively.

2,2′-Dicarboxy-$\Delta^{9,9'}$-bifluorene (Va) was found to be too insoluble and difficult to purify for resolution. In search for a more soluble derivative of this acid the preparation of the ditetrahydrofurfuryl ester by the dehydrogenation of ditetrahydrofurfuryl bifluoryldicarboxylate (VI, R = tetrahydrofurfuryl), with chloranil was tried. The reaction which was carried out successfully with the diethyl ester (VI, R = C_2H_5) failed for this example. Synthesis of esters of optically active alcohols of 2,2′-dicarboxy-$\Delta^{9,9'}$-bifluorene by the steps used for the ethyl ester were not tried since the products from 9,9′-dichlorofluorene-2-carbonyl chloride and 2-octanol, *sec*-butyl alcohol, menthol, and tetrahydrofurfuryl alcohol were oils and were difficult to purify.

4,4′-Dicarboxy-$\Delta^{9,9'}$-bifluorene (Vb) formed a salt with *d*-α-phenylethylamine which by crystallization from acetone gave two fractions. The more insoluble salt gave specific rotations varying from +17.4° to +21.1°. The more soluble fraction gave specific rotations varying from 0 to −9.8°. Acids (Vb) liberated from these salts due to the deep red colors of their solutions in ammonium hydroxide, in dimethylformamide, and in a mixture of phenol, water, and acetone could only be studied polarimetrically at very dilute concentrations. Observed readings in a two-decimeter tube under these conditions were no larger than 0.06° and were difficult to duplicate when taken by three different observers. The results obtained in ammonium hydroxide would point to resolution but the readings were taken, however, by only one observer.

This problem is being studied further with the use of a photoelectric polarimeter.

EXPERIMENTAL[3]

9,9-Dichlorofluorene-2-carbonyl chloride (IIa). Finely divided fluorenone-2-carbonyl chloride (5) (25 g.) was mixed with phosphorus pentachloride (25 g.) and heated at 150° for three hours. The phosphorus oxychloride formed was removed by distillation and the residue heated an additional hour at 170–175°. Crystallization of the resulting solid from petroleum ether (b.p. 60–68°) gave a pale yellow solid; m.p. 147–149°; yield 29.1 g. (95%).

Anal. Calc'd for $C_{14}H_7Cl_3O$: C, 56.50; H, 2.37.

Found: C, 56.28; H, 2.48.

9,9-Dichloro-2-carbethoxyfluorene (IIIa). 9,9-Dichlorofluorene-2-carbonyl chloride (14.5 g.) was dissolved in absolute ethanol (100 ml.) by heating at 100° for 15 minutes. The resulting solution, after standing for 45 minutes, was cooled and the crystals were filtered. Crystallization from petroleum ether (b.p. 60–68°) gave a solid melting at 119–120°; yield, 13.0 g. (87.5%).

---

[2] After the completion of this work, Bell, *J. Chem. Soc.*, 5047 (1952) has published the synthesis of 4,4′-dicarboxy-$\Delta^{9,9'}$-bifluorene by reactions similar to those used in this work. He reported the compound as too highly colored for polarimetric observation.

[3] Melting points are not corrected.

Anal. Calc'd for $C_{16}H_{12}Cl_2O_2$: C, 62.7; H, 3.9.
Found: C, 62.7; H, 3.96.

The use of 2-octanol, 1-menthol, *sec*-butyl alcohol, and tetrahydrofurfuryl alcohol in place of the ethanol gave only oils.

2,2′-Dicarbethoxy-$\Delta^{9,9'}$-bifluorene (IVa). A solution of 2-carbethoxy-9,9-dichlorofluorene (10 g.) in xylene (200 ml.) was refluxed with copper powder (30 g.) for 9 hours under nitrogen. The hot solution was filtered and the copper was washed with xylene until the washings were colorless. The combined xylene solutions when concentrated to a small volume (40 ml.) and cooled, gave the red diester; m.p. 196–202°; yield, 4.4 g. (55%). Recrystallization from ethanol gave a sample melting at 204–206°.

Anal. Calc'd for $C_{32}H_{24}O_4$: C, 81.4; H, 5.08.
Found: C, 80.6; H, 5.19.

Diethyl 9,9′-bifluoryl-2,2′-dicarboxylate (6) (0.5 g.) in toluene (35 ml.) was refluxed with chloranil (0.26 g.) for 4 hours. The red solution after concentration and removal of the chloranil by filtration gave 2,2′-dicarbethoxy-$\Delta^{9,9'}$-bifluorene (0.1 g.).

A dioxane solution of this ester upon standing for two weeks at room temperature open to the air, changed from a deep orange color to a yellow one and gave upon pouring into water 2-carbethoxyfluorenone. This sample gave no lowering in melting point when mixed with a sample synthesized from fluorenone-2-carbonyl chloride.

2-Carbethoxyfluorenone. Fluorenone-2-carbonyl chloride (2 g.) was heated with ethanol (15 ml.) at 100° for 15 minutes. The bright yellow prisms obtained upon cooling melted at 140°; yield, 1.9 g. (91%).

Anal. Calc'd for $C_{16}H_{12}O_3$: C, 76.2; H, 4.76.
Found: C, 75.5; H, 4.67.

2,2′-Dicarboxy-$\Delta^{9,9'}$-bifluorene (Va.) 2,2′-Dicarbethoxy-$\Delta^{9,9'}$-bifluorene (2.2 g.) was refluxed under nitrogen in a solution of water (60 ml.) and ethanol (120 ml.) containing potassium hydroxide (5 g.) for two hours. The resulting clear solution was poured onto ice, acidified with dilute hydrochloric acid, and filtered. The dark red compound (1.7 g.) (88%) melted above 350° and was insoluble in hot acetic acid and toluene. Recrystallization from dimethylformamide gave red crystals.

Anal. Calc'd for $C_{28}H_{16}O_4$: C, 80.8; H, 3.85.
Found: C, 79.7; H, 4.10.

Ditetrahydrofurfuryl 9,9′-bifluoryl-2,2′-dicarboxylate. Finely ground 9,9-bifluoryl-2,2′ carbonyl chloride (6) (1.5 g.) was refluxed with tetrahydrofurfuryl alcohol (7.5 ml.) for 15 minutes. The solution upon cooling gave creamy white crystals, m.p. 217–222°; yield 1.1 g. (67%).

Anal. Calc'd for $C_{38}H_{34}O_6$: C, 77.8; H, 5.8.
Found: C, 76.5; H, 6.0.

This ester when refluxed with chloranil in toluene for 16 hours under nitrogen gave a red solution from which only starting material could be isolated.

4,4′-Dicarbethoxy-$\Delta^{9,9'}$-bifluorene (IVb). Coupling of 4-carbethoxy-9,9-dichlorofluorene (7) (8 g.) was accomplished by refluxing in benxene (30 ml.), with copper powder (16 g.). Removal of the benzene gave red crystals (3.5 g.) melting at 238–241°. Three recrystallizations from benzene gave a sample melting at 242–244°.

Anal. Calc'd for $C_{32}H_{24}O_4$: C, 81.4; H, 5.08.
Found: C, 81.21; H, 5.45.

A solution of the ester (0.35 g.) in dioxane (35 ml.) when allowed to stand open to the air for two weeks became pale yellow and gave upon pouring into water 4-carbethoxyfluorenone (0.33 g.). After two recrystallizations from ethanol the ester melted at 101–102° and proved identical with an authentic sample (7).

4,4′-Dicarboxy-$\Delta^{9,9'}$-bifluorene (Vb). This acid was prepared in a manner similar to that used for the 2,2′-isomer; the yield of red solid was theoretical. After two recrystallizations from a mixture of acetic acid and xylene red crystals were obtained melting at 315–318°.

Anal. Calc'd for $C_{28}H_{16}O_4$: C, 80.9; H, 3.85.
Found: C, 80.45; H, 4.41.

A solution of the acid (0.3 g.) in dioxane (25 ml.) turned yellow when allowed to stand open to the air for a month. Upon pouring into water 4-carboxyfluorenone (0.25 g.) was obtained melting at 223–225° and was found to be identical with an authentic sample (8).

Studies on the resolution of 4,4′-dicarboxy-$\Delta^{9,9'}$-bifluorene. The acid (2.0 g.) was placed in a Soxhlet cup and extracted with acetone (200 ml.) containing *d*-α-phenylethylamine (1.4 ml.). The orange solid which separated from the hot acetone solution was filtered and washed with acetone; m.p. 175–190°; yield, 0.89 g.

Anal. Calc'd for $C_{36}H_{27}NO_4$: N, 4.26. Found: N, 4.35.

A sample (0.1007 g.) in absolute ethanol (25 ml.) in a two-decimeter tube gave an observed reading which varied from +0.14 to +0.17° for three separate observers; temp. 23.5°. These values correspond to specific rotations of +17.4° and +21.1° respectively.

The salt was treated in two ways: (*a*) The sample was dissolved in 6 *N* ammonium hydroxide and treated with cooling with dilute hydrochloric acid. The precipitate was filtered and washed with water, dilute hydrochloric acid, and ether. It was then dried at 100° for an hour. A sample (0.0132 g.) in 6 *N* ammonium hydroxide (10 ml.) gave a reading of +0.023° or a specific rotation of [α] +17.3° (one observer). (*b*) A sample of the salt was dissolved in ethanol and acidified with cooling with dilute hydrochloric acid. The precipitate was filtered, washed with water, and air-dried. The product (0.0712 g.) in dimethylformamide (25 ml.) in a two-decimeter tube gave the following readings; −0.03°, +0.01°, +0.01° when viewed by three observers.

The hot acetone filtrate on cooling gave a solid salt (0.5 g.) melting at 178–190°. A sample (0.1229 g.) in absolute ethanol (25 ml.) in a two-decimeter tube at 25° gave observed readings of +0.086° and +0.097° for two independent readers. These values correspond to specific rotations of +8.8° and +9.8° respectively. This salt when dissolved in ethanol and acidified with dilute hydrochloric acid gave a sample (0.0327 g.) which in a mixture of 95% phenol (30 ml.) and acetone (12 ml.) in a two-decimeter tube gave readings of −0.01°, −0.03°, and −0.06° (three observers).

Another separate resolution gave a salt (0.0606 g.) which in ethanol (10 ml.) gave an observed reading of 0° (one observer).

Anal. Calc'd for $C_{36}H_{27}NO_4$: N, 4.26. Found: N, 4.54.

The phenylethylamine salt with a rotation of 0° when converted into the acid by dissolving in ammonium hydroxide in the same manner as the *d*-salt gave an acid (0.0242 g.) which in 6 *N* ammonium hydroxide (10 ml.) in a one-decimeter tube showed a rotation of −0.046° or a specific rotation of [α] −19.0° (one observer).

All readings were made using a mercury vapor lamp alone and with a Wratten filter No. 29 (red). The absorption spectra of the diethyl ester indicated transparency at a wave length greater than 525 mμ. The sodium vapor lamp was not an intense enough source of light to give good readings. The readings for the two methods used varied very little from each other.

The amorphous nature of the precipitated acids, their high melting points, and their insolubility made it impossible to use these physical properties to supplement the above low optical rotations.

SUMMARY

The synthesis of 2,2′-dicarboxy-$\Delta^{9,9'}$-bifluorene and 4,4′-dicarboxy-$\Delta^{9,9'}$-bifluorene, their ethyl esters, and the α-phenylethylamine salts of the 4,4′-diacid are described.

Studies on the resolution of 4,4′-dicarboxy-$\Delta^{9,9'}$-bifluorene are inconclusive due to the difficulties encountered in making measurements with the highly colored solutions.

Iowa City, Iowa

REFERENCES

(1) Bergmann and Weizman, *Chem. Revs.*, **29**, 575 (1941).
(2) Wawzonek and Fan, *J. Am. Chem. Soc.*, **68**, 2541 (1946).
(3) Fenimore, *Acta Cryst.*, **1**, 295 (1948).
(4) Bergmann, Berthier, Pullman, and Pullman, *Bull. soc. chim.*, 1081 (1950).
(5) Ray and Rieveschl, *J. Am. Chem. Soc.*, **65**, 836 (1943).
(6) Ray, Weisburger, and Weisburger, *J. Org. Chem.*, **13**, 655 (1948).
(7) Graebe and Aubin, *Ann.*, **247**, 275 (1888).
(8) Stobee and Seydel, *Ann.*, **370**, 137 (1909).