FULVENES AND THERMOCHROMIC ETHYLENES—XLII¹

THE CONFORMATION OF BIANTHRONE AND DIXANTHYLENE

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THE reversible thermochromism of bianthrone (I) (yellow rightarrow green) and dixanthylene (II) (colorless rightarrow blue green) has been known for some time,² but until now no generally accepted theory has been put forward for this interesting phenomenon. Grubb and Kistiakowsky³ and Theilacker *et al.*⁴ have shown unequivocally that the two differently coloured forms are different molecular species; equally, it has been recognised that the phenomenon is related to the mutual interference of the four hydrogen atoms in the immediate vicinity of the double bond. In the latter respect, it is noteworthy that the substitution of at least two of these four hydrogen **a**toms destroys the thermochromism of the systems I and II.

For the structure of the two forms of I and II various suggestions have been made. Some authors have assumed that the colourless form is planar, some that the coloured form corresponds to this conformation. In the solid state,⁵ bianthrone (I) is nonplanar, but has a centre of symmetry. Obviously, this result need not apply necessarily to the conformation of the compound in solution.

After we have shown by dipole moment and NMR measurements⁶ that in the analogously built dibiphenylene-ethene (III) which has in the solid state a structure very similar to I⁷, the two halves of the molecule lie in different planes, it seemed of interest to seek information about the conformation of I and II by the determination of the dipole moments of suitable polar-substituted derivatives of these systems. If the structure of the two dixanthylene derivatives VII and VIII is that of a classical *trans*-compound, their moments would be zero, if it were that of a classical *cis*-compound, the moments would have maximum values—the moments of intermediary, i.e. non-classical, non-planar conformations would lie between these two extreme figures. From the moments observed (Table 1), the angles of twist were calculated to be 93° and 89°, respectively.

In these calculations it is assumed in accordance with Kortüm and Buck⁸ that

¹ Part XLI : H. Weiler-Feilchenfeld, I. Agranat and E. D. Bergmann, *Trans, Farady Soc.* in press (1966).

⁹ For reviews of the subject, see E. D. Bergmann, *The Fulvenes in Progress of Organic Chemistry* Vol. III; p. 481. Butterworths, London (1955); See T. H. Day, *Chem. Revs.* 63, 65 (1963).

⁸ W. T. Grubb and G. B. Kistiakowsky, J. Amer. Chem. Soc. 72, 419 (1952).

⁴ W. Theilacker, G. Kortuem and H. Ellieausen, Chem. Ber. 89, 2306 (1956).

⁵ E. Harnik and G. M. J. Schmidt, J. Chem. Soc. 3295 (1954).

⁶ M. Rabinowitz, I. Agranat and E. D. Bergmann, Tetrahedron Letters 1265 (1965).

⁷ S. C. Nyburg, Acta Cryst. 7, 779 (1954).

⁸ G. Kortüm and M. Buck, Z. Elektrochem. 60, 53 (1956).

the moments of the parent substances I and II are zero. The small moments reported by Bergmann and Fischer⁹ are probably only apparent, as those compounds will show at least a certain amount of exalted distortion polarization.¹⁰

The situation is, however, more complex than the above simple calculation would lead one to expect. Obviously, the finite dipole moments of the dixanthylene (VII, VIII) and the bianthrone derivatives (IV, V, VI) show beyond doubt that the molecules are not centrosymmetric (and, therefore, most probably not planar); however, a definite structural assignment is impossible as a brief discussion of the moments of the bianthrone derivatives (IV-VI) will show. Whilst the moment of 3.30 for IV could still be explained by a planar *cis*-structure (relative to the bromine atoms) although the value is *too large* for that—substances V and VI should have zero

μ(D)
3.30
1.88
1.87
2.00
2.07

TABLE 1. DIPOLE MOMENTS

moments in *every* planar or non-planar configuration, as long as each half of the molecule is planar; the two C-halogen moments will always cancel each other out. It must, therefore, be assumed that both halves of the molecules (or at least one of them) are distorted so that the C-halogen moments are not parallel and in opposite directions. It may also be possible that these substituted bianthrones show a high distortion polarization; if one, e.g., would explain the moments of V and VI in this manner, then the moment of IV caused by the two C-Br bonds, would be $3\cdot30-1\cdot87-1\cdot43$ D, indicating an angle of twist of $125 (\pm 20^\circ)$ between the two(planar) halves of the biplanar molecule.

Obviously, the values of the angles constitute only crude approximations, but it seems clear that the molecules of I and II in their colourless state are not monoplanar.

For the synthesis of the compounds IV-VIII, well-known unambiguous methods have been used. From 4,5-dimethylphthalic anhydride¹¹ and bromobenzene in the presence of aluminium chloride, 2-(4-bromobenzoyl)-4,5-dimethylbenzoic acid (IX) was obtained. Catalytic reduction of the carbonyl group proved possible only under conditions which also led to hydrogenolytic removal of the bromine atom. It was, therefore, necessary to carry out the reduction to 2-(4-bromobenzyl)-4,5-dimethylbenzoic acid (XI) in two steps: reduction with amalgamated zinc and hydrochloric acid to the corresponding lactone (X) and treatment of the latter with phosphorus and hydroiodic acid. From XI, 7-bromo-2,3-dimethylanthrone (XII) was easily obtained by cyclodehydration, and the ketone was successively dehydrogenated to the bianthronyl derivative (XIIa) and the yellow bianthrone (IV), which is strongly thermochromic.

For the preparation of V and VI, the first step was the condensation of cumene

- * E. D. Bergmann and E. Fischer, Bull. Soc. Chim. Fr. 1084 (1950).
- ¹⁰ E. D. Bergmann, E. Fischer and J. Jaffe, J. Amer. Chem. Soc. 75, 3230 (1953).
- ¹¹ S. Sugasawa and N. Sugimoto, J. Pharm. Soc. Japan 61, 62 (1941).

with 3-fluorophthalic¹² and 3-chlorophthalic anhydride¹³. Activated zinc and ammonia reduced the fluorinated keto acid (XIIIa) to the corresponding 3-fluoro-2-(4-isopropylbenzyl) benzoic acid (XIVa), whilst for the corresponding chloro compound (XIIIb) the treatment with phosphorus and hydroiodic acid in boiling propionic acid was found preferable. Hydrofluoric acid cyclized XIV to XV (a,b); these anthrones were then dehydrogenated in two steps, as above, to V and VI.

For the synthesis of the two dixanthylenes (VII, VIII), the classical method,¹⁴ viz. the reduction of 2- and 3-chloroxanthone with zinc dust and hydrochloric acid in boiling glacial acetic acid was employed.



EXPERIMENTAL

4,5-Dimethylphthalic anhydride.¹¹ 4,5-Dimethyl-1,2,3,6-tetrahydrophthalic anhydride was obtained in quantitative yield from 2,3-dimethylbutadiene and maleic anhydride and melted after recrystallization from pet. ether (60-80°) at 78°.¹⁵ A mixture of 90 g of this anhydride and 32 g of S was heated at 240°, until no more H₈S was evolved (5 hr), and the product distilled directly (b.p. 118-123° (20 mm)) and recrystallized from xylene, m.p. 206°; yield, 55 g (62%).

¹³ A. Heller, J. Org. Chem. 25, 834 (1960).

- ¹³A. A. Ponomarenko, J. Gen. Chem. S.S.S.R. 20, 469 (1950).
- ¹⁴G. Gurgenjanz and St. v. Kostanecki, Ber. Dtsch. Chem. Ges. 28, 2310 (1895).
- ¹⁵ E. H. Farmer and F. L. Warren, J. Chem. Soc. 897 (1929).

2-(p-Bromobenzoyl)-4,5-dimethylbenzoic acid (IX). In small portions, 29 g AlCl₃ was added to a solution of 17.6 g 4,5-dimethylphthalic anhydride in 60 ml bromobenzene and the mixture heated at 70° for 5 hr and decomposed with ice and HCl. The excess of bromobenzene was removed by steam distillation and the solid product recrystallized successively from glacial AcOH and toluene, m.p. 231°; yield, 20 g (60%). (Found: C, 57.1; H, 4.4. C₁₆H₁₃BrO₃ requires: C, 57.6; H, 3.9%.)

Methyl ester, prepared in dioxan with ethereal diazomethane solution, from MeOH or cyclohexane, m.p. 131°. (Found: C, 58.9; H, 4.4. Calc. for $C_{17}H_{18}BrO_8$; C, 58.8; H, 4.3%.)

Substances	Solvent	Temp	ε,	<i>v</i> ₁	α'	β'	P∞	R _{calc} .	μ
2,2'-Dichloro-	_								
dixanthylene (VII) 3,3'-Dichloro-	benzene	30°	2.2656	1.1524	7.32	-2.52	196·8	116-5	2.00
dixanthylene (VIII) 5,5'-Dichloro- 2,2'-diisopropyl-	benzene	30°	2.2655	1.1524	8.00	-2.70	202.8	116-5	2.07
bianthrone (VI) 5,5'-Difluoro-	benzene	30°	2.2645	1.1461	5.64	-1.96	220.4	150-2	1-87
bianthrone (V) 7,7'-Dibromo-	benzene	30°	2.2644	1.1514	5.32	1.72	211-2	140-0	1.88
2,2'3,3'-tetra- methylbianthrone (IV)	<i>p</i> -xylene + <i>p</i> -dichloro- benzene	52°	2.3343	0-9391	11.8	-1·28	351.0	146-6	3.30

TABLE 2

2-Benzyl-4,5-dimethylbenzoic acid. At 80°, a solution of 10 g of the foregoing keto acid in 150 ml glacial AcOH and 3 ml 60% perchloric acid was hydrogenated in the presence of 1 g Pd-C (10%) as catalyst. The absorption of H₂ ceased after 4 hr. The filtered solution was diluted with an equal volume of water and the precipitate filtered and recrystallized from toluene, m.p. 192°; yield, 6 g (82%). (Found: C, 80.0; H, 6.8. $C_{19}H_{16}O_2$ requires: C, 80.0; H, 6.7%.)

2-(p-Bromo- α -hydroxybenzyl)-4,5-dimethylbenzoic acid lactone (X). A mixture of 33 g ZnHg, 70 ml conc. HCl, 24 g water, 24 g IX and 80 ml benzene was refluxed with stirring for 20 hr and the solution, while still hot, filtered from the undissolved metal and some high-melting organic material. The filtrate was evaporated to dryness and the residue extracted with 90 ml 10% Na₂CO₃aq, filtered, dried and recrystallized from methylcyclohexane, m.p. 147°; yield, 14 g (61%). (Found: C, 61·0; H, 4·3. Calc. for C₁₆H₁₈BrO₃: C, 60·6; H, 4·1%.)

2-(p-Bromobenzyl)-4,5-dimethylbenzoic acid (XI). A mixture of 12 g of the foregoing lactone, 3 g I₁, 1.5 g red P, 40 ml glacial AcOH and 1.5 ml water was refluxed, with stirring, for 8 hr and the filtered solution cooled and poured into a 5% NaHSO₂aq. The precipitate was extracted with 300 ml boiling 10% Na₂CO₂aq. Upon cooling, the sodium salt of the desired acid crystallized out. Acidification gave the free acid, white needles of m.p. 173-174° (9.6 g; 80%); the m.p. was not raised by recrystallization from methylcyclohexane. (Found: C, 60.3; H, 5.2. Calc. for : C₁₀H₁₅BrO₁: C, 60.2; H, 4.7%.)

7-Bromo-2,3-dimethylanthrone (XII). A mixture of 9 g of the foregoing acid and 27 g conc. H_sSO₄ was stirred at 10° until a homogeneous solution resulted which was poured onto crushed ice. The yellowish product was filtered, dried and recrystallized from toluene, m.p. 202-203°, yield, 7 g (82%); λ_{max}^{EtoH} 277 m μ (4·17); 306 m μ (4·00), whilst anthrone¹⁶ shows λ_{max} 258 (4·20) and 308 m μ (shoulder; 3·60). (Found: C, 63·8; H, 4·3. Calc. for C₁₆H₁₉BrO: C, 64·2; H, 4·3%.)

7,7'-Dibromo-2,2',3,3'-tetramethylbianthronyl (XIIa). A solution of 5 g FeCl₃ in 5 ml water was added to a boiling suspension of 5.5 g XII in 50 ml glacial AcOH. The crystals of the anthrone disappeared quickly, and the colourless product began to precipitate. After 15 min, the solution was cooled and the precipitate filtered off, washed with water and glacial AcOH and recrystallized from 300 ml xylene. The product (4.1 g; 75%) decomposed at 250° without melting. (Found: C, 64.3; H, 3.9. Calc. for $C_{32}H_{34}Br_{3}O_{3}$: C, 64.0; H, 4.0%.)

¹⁰ R. N. Jones, J. Amer. Chem. Soc. 67, 2127 (1945).

7,7'-Dibromo-2,2',3,3'-tetramethylbianthrone (IV). In a N₂ atmosphere, 4.0 g of XIIa was dissolved in a solution of 4.0 g KOH in 50 ml anhydrous alcohol and the dark-red solution poured into cold, dil HCl. The 7,7'-dibromo-2,2',3,3'-tetramethylbianthranol so obtained was filtered off, dried in a dessicator and dissolved in the minimum quantity of dioxan. When 4 g p-benzoquinone dissolved in acetone was added to this solution, the desired product began to crystallize immediately. After 0.5 hr the yellow, strongly thermochromic crystals were collected and recrystallized from xylene. They did not melt below 340°; yield, 2.4 g (60%); λ_{max}^{ohil} 244 (4.62); 324 (4.06); 412 m μ (4.26); $\#_{max}^{BBr}$ 1670 cm⁻¹, whilst bianthrone shows λ_{max} 255 (4.20), 385 (4.20)¹⁷ and ν_{max} 1687 cm⁻¹.¹⁸ (Found: C, 64.5; H, 4.0. Calc. for C₂₂H₂₂Br₃O₃: C, 64.2; H, 3.7%.)

3-Fluoro-2-(p-isopropylbenzoyl) benzoic acid (XIIIa). With stirring and at a temp not exceeding 45°, 55 g AlCl₂ was added to a mixture of 30 g 3-fluorophthalic anhydride¹³ and 250 ml cumene. The reaction was completed by heating the mixture at 50° for 1 hr and the product decomposed by addition to 500 g ice and 20 ml conc. HCl. The aqueous layer was extracted successively with 200 ml benzene and 100 ml ether, and the combined organic layers were washed with 300 ml water and extracted 3 times with 200 ml 6% Na₂CO₂aq. The alkaline solution was extracted with benzene and then acidified with 5N HCl. The keto acid precipitated as an oil, but crystallized quickly upon trituration with MeOH. After 2 recrystallizations from benzene–cyclohexane (4:1), the acid (20 g; 39%) melted at 116°. (Found: C, 71·3; H, 5·8; F, 6·5. Calc. for: $C_{17}H_{18}FO_{3}$: C, 71·3; H, 5·3; F, 6·5%.)

3-Fluoro-2-(p-isopropylbenzyl) benzoic acid (XIVa). A mixture of 20 g of the foregoing acid, 250 ml 25% NH₄OH, 55 g of Zn dust and a few drops ammoniacal CuSO₄ was refluxed for 2 hr and, after addition of 200 ml 10% Na₂CO₂aq and some CuSO₄ solution, for another 16 hr. Acidification of the filtered solution with HCl gave the desired acid (14.5 g; 76%), m.p. 99–100° after recrystallization from ligroin. (Found: C, 74.7; H, 6.1. Calc. for $C_{17}H_{17}FO_4$: C, 75.0; H, 6.2%.)

5-Fluoro-2-isopropylanthrone (XVa). During 30 min a mixture of 4 g of the foregoing acid and 40 g anhydrous HF was kept in an ice bath and then the HF allowed to evaporate. The oily residue was treated with Na₂CO₂aq whereupon it crystallized. From MeOH, yellowish crystals, m.p. 80° (2.5 g; 63%) were obtained. (Found: C, 79.7; H, 5.9. Calc. for $C_{17}H_{18}FO$: 80.3; H, 5.9%.)

5,5'-Difluoro-2,2'-di(isopropyl) bianthronyl. A mixture of 1.5 g XVa in 10 ml glacial AcOH and of 0.2 g AcONa and 1.5 g FeCl₃ in 1.5 ml water was heated at 90° for 30 min and refluxed for 1 hr. Although part of the product crystallized on cooling, the mixture was diluted with an equal volume of MeOH and the product (0.85 g; 56%) recrystallized from EtOH, m.p. 153–154°. (Found: C, 80.8; H, 5.5. Calc. for $C_{14}H_{18}F_{1}O_{1}$: C, 80.6; H, 5.5%.)

5,5'-Difluoro-2,2'-di(isopropyl) bianthrone (V). A mixture of 0.75 g of the foregoing compound in 10 ml abs. EtOH and 0.9 g KOH was refluxed in an atmosphere of N₁ for 2 hr, and then poured onto 6 g ice and 3.5 ml conc. HCl. As only very little of the expected 5,5'-difluoro-2,2'-di(isopropyl) bianthranol precipitated, 25 ml EtOH, 20 ml water and an acetone solution of 1 g p-benzoquinone was added. The desired diketone (0.65 g; 85%) crystallized at once; it was washed with a mixture (3:2) of acetone and water and recrystallized from butanol or glacial AcOH or purified by chromatography on alumina, CHCl₂ serving as eluent. The yellow product, m.p. 249°, showed only weak thermochromism and gave an intensely blue colour reaction with conc. H₂SO₄. (Found: C, 81.0; H, 5.7. Calc. for $C_{24}H_{26}F_2O_3$: C, 80.9; H, 5.2%.)

3-Chloro-2-(p-isopropylbenzoyl) benzoic acid (XIIIb). In small portions and at room temp, 310 g AlCl₂ was added, with stirring, to a suspension of 182 g 3-chlorophthalic anhydride¹³ (m.p. 129°, from benzene-pet. ether) in 1 l. cumene. After one further hr, the reaction mixture was treated with 1.5 kg ice and 100 ml conc. HCl. The excess cumene was removed by steam distillation and the oily organic residue treated with MeOH. From toluene, leaflets crystallized, m.p. 105°; yield, 194 g (74%). (Found: C, 67.5; H, 5.0; Cl, 12.2. Calc. for C₁₇H₁₄ClO₃: C, 67.5; H, 5.0; Cl, 11.8%.)

3-Chloro-2-(4-isopropylbenzyl) benzoic acid (XIVb). A mixture of 20 g of the foregoing acid, 200 g propionic acid, 10 g red P, 10 g I₁, 20 g NaI and 6 ml water was refluxed for 60 hr and poured into 300 ml 5% aqueous sodium metabisulphite. The acid was recrystallized from pet. ether, m.p. 128°, yield, 16 g (85%). (Found: C, 70.4; H, 6.0. Calc. for $C_{17}H_{17}ClO_1$: C, 70.7; H, 5.9%.)

5-Chloro-2-isopropylanthrone (XVb). A mixture of 18.5 g of the foregoing acid and 100 ml anhydrous HF was kept in a closed vessel for 12 hr; then the acid was evaporated and the residue

¹⁷ W. Theilacker, G. Kortuem and G. Friedheim, Ber. 83, 508 (1950).

¹⁸ M.-L. Josien and N. Fuson, Bull. Soc. chim. France, 389 (1952).

treated with 5% Na₂CO₂aq, filtered and recrystallized from MeOH yielding 14 g of the anthrone (80%), m.p. 115°. (Found: C, 75'3; H, 5'7. Calc. for $C_{17}H_{18}ClO$: C, 75'6; H, 5'6%.)

5,5'-Dichloro-2,2'-diisopropylbianthronyl. A solution of 10 g FeCl₃ in 10 ml water was added to a solution of 10 g anthrone in 25 ml hot glacial AcOH and the mixture heated on the water-bath for 15 min. The pure product (9 g; 90%), m.p. 210° crystallized upon cooling, λ_{max}^{BtOH} 270 m μ (log ε 4.40). (Found: C, 75.7; H, 5.2. Calc. for C₃₄H₃₅Cl₂O₃: C, 75.8, H, 5.2%.)

5,5'-Dichloro-2,2'-diisopropylbianthrone (VI). In a N₂ atm, 9 g of the foregoing compound was refluxed for 3 hr in 100 ml 5% ethanolic KOH. The orange-red solution was decanted from unchanged starting material (3 g) and quickly neutralized with alcoholic HCl. Then 9 g p-benzoquinone in anhydrous acetone was added and the mixture kept at room temp for 24 hr. The precipitate was filtered off, washed successively with water and acetone and recrystallized from xylene, m.p. above 300°; yield, 5 g (83%, calc. on the material entered into reaction); $\lambda_{max}^{OBCl} 273$ (4·46); 300 (4·26); 392 m μ (3·30), \tilde{r}_{max}^{EBr} 1430, 1466, 1600, 1670 cm⁻¹. (Found: C, 76·1; H, 5·2. Calc. for C₂₄H₃₆Cl₂O₃: C, 76·1; H, 5·0%.)

2-Chloroxanthone was prepared according to Dhar¹⁹ in 43% yield. After recrystallization from EtOH, it melted at $171-172^{\circ}$ (lit: $165^{\circ 19}$, $171^{\circ 0}$.)

2,2'-Dichlorodixanthylene (VII). Following the classical method for the preparation of dixanthylene,¹⁴ a mixture of 7 g 2-chloroxanthone, 50 ml glacial AcOH, 3 g Zn dust and a few drops of conc. HCl was refluxed for 5 hr; from time to time, small quantities of conc. HCl were added. The solid was filtered and recrystallized from xylene, m.p. 308° (lit.³¹: 304°); yield, 3.5 g (56%). (Found: C, 72.6; H, 3.1; Cl, 16.7. Calc. for C₁₈H₁₄Cl₂O₂: C, 72.7; H, 3.3; Cl, 16.6%.) $\lambda_{\text{max}}^{\text{chlr}} 255^{\circ}$ (4.13); 286 (4.00); 374 m μ (4.23). Fluorescence spectrum (in benzene): 444 and 457 m μ .

3-Chloroxanthone was prepared according to Goldbery and Wragg.**

3,3'-Dichlorodixanthylene (VIII) was obtained in the same manner as the 2,2'-isomer; yield, 58%. After recrystallization from xylene, it melted at 294° (dec). (Found: C, 73.0; H, 3.4; Cl, 16.7. Calc. for C₃₅H₁₄Cl₈O₃: C, 72.7; H, 3.3; Cl, 16.6%.) λ_{max}^{Chif} 274 (4.45); 295° (4.22); 332 (3.96); 345 (4.06); 397° (4.04); 417 (4.15); 437 m μ (4.11); fluorescence spectrum (in benzene): 471 and two shoulders at 438 and 505 m μ .

The dipole moments were determined according to Halverstadt and Kumler.33

¹⁰ S. N. Dhar, J. Chem. Soc., 117, 1053 (1920).

- ²⁰ F. Ullmann and C. Wagner, Liebigs Ann. 355, 359 (1907); 371, 388 (1909).
- ¹¹ A. Schoenberg, A Mustafa and M. Ezz El Din Sobhy, J. Amer. Chem. Soc. 75, 3377 (1955).
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- 23 I. F. Halverstadt and W. D. Kumler, J. Amer. Chem. Soc. 64, 2988 (1942).