curiferrocene with either ethanolic sodium iodide or aqueous sodium thiosulfate solution are mixtures of linear polymercuriferrocenylenes possibly containing cyclic polymers. By analogy to other mercury containing ring systems[7,29,30] the value of x is probably very low.

[29] G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 883 (1958).

[30] G. Wittig, E. Hahn, and W. Tochtermann, *ibid.*, **95**, 431 (1962).

Fulvenes and Thermochromic Ethylenes. XXXIII.[1] Polycyclic Derivatives of Heptafulvene

ERNST D. BERGMANN AND RAFAEL IKAN

Department of Organic Chemistry, Hebrew University, Jerusalem, Israel

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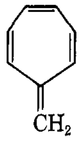
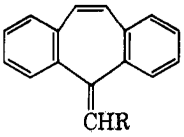
Four polycyclic heptafulvenes (III, IV) have been synthesized, and their spectra and dipole moments have been measured. The data are compared with the theoretical predictions.

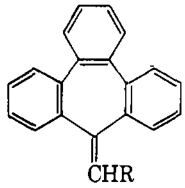
It has been calculated[2a,b] that anellation of benzene rings to the system of heptafulvene (I) will first produce a hypsochromic effect which will change into a bathochromic one upon addition of even more rings. Furthermore, phenyl substitution at the exocyclic carbon atom of I will, on the one hand, increase the polarity of the semicyclic double bond, and, on the other hand, cause a hypsochromic shift. As the experimental results as yet have not borne out the theory,[3] the most complex benzologs of I prepared so far being the 1-methylene-2,3,6,7-dibenzocyclohepta-2,4,6-triene (II) and 1-methylene-2,3,4,5,6,7-tribenzocyclohepta-2,4,6-triene[4] (IIa) type, it seemed of interest to study some higher benzologs and the corresponding heptafulvene ketones.



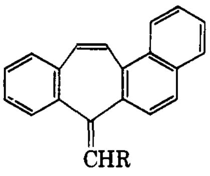
I



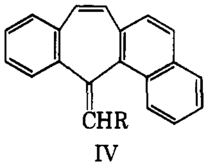
II



IIa

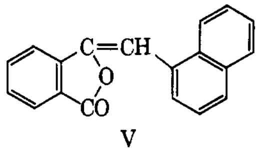


III

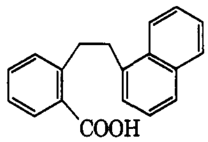


IV

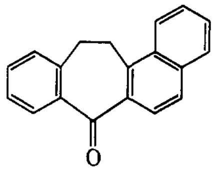
Four heptafulvenes of type III and IV have now been prepared. The synthesis followed the route used[5-7] for the preparation of 2,3,6,7-dibenzocyclohepta-2,4,6-trien-1-one (as II). From phthalic anhydride and 1-naphthylacetic acid, (1-naphthylmethylene)phthalide (V) was obtained. Its reduction with phosphorus and hydriodic acid gave *o*-[β-(1-naphthyl)ethyl]benzoic acid (VI) which was cyclized with polyphosphoric acid to the ketone VII. Successive treatment with bromine and pyridine converted the latter into 8,9-benzo-7-oxo-*7H*-cyclohepta[*a*]naphthalene (VIII). Analogously, the isomeric 9,10-benzo-11-oxo-11*H*-cyclohepta[*a*]naphthalene (IX) was synthesized starting from 2-naphthylacetic acid.



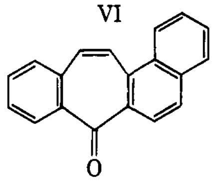
V



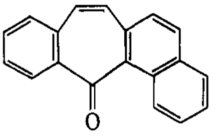
VI



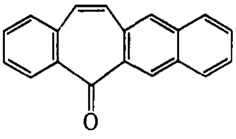
VII



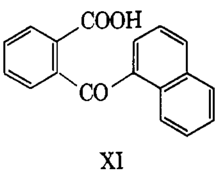
VIII



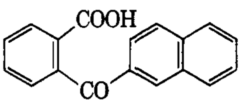
IX



X



XI



XII

In the cyclization of *o*-[β-(2-naphthyl)ethyl]benzoic acid, the H isomer of VI, theoretically IX or X, could be formed, depending on whether the reaction leads from position 2 to 1 or 3 of the naphthalene nucleus. Although the former alternative, and thus IX seemed more likely, an exact proof was considered necessary. Ozonization of the heptafulvene ketone led to a dicarboxylic acid which upon thermal decarboxylation yielded *o*-(1-naphthoyl)benzoic acid (XI), identical with an authentic sample. This is consistent with formula IX; in this sequence of reactions X would have given *o*-(2-naphthoyl)benzoic acid (XII).

It is interesting to note that there is no large difference in the carbonyl frequency (potassium bromide

[1] Part XXXII: E. D. Bergmann, A. Heller, and H. Weiler-Feilchenfeld, *Bull. soc. chim. France*, 635 (1959).

[2] (a) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, **47**, 484 (1959); (b) E. D. Bergmann, *et al.*, *Bull. soc. chim. France*, **18**, 684 (1951).

[3] See E. D. Bergmann, "Progress of Organic Chemistry," Vol. 3, Butterworths Publications, Ltd., London, 1955, p. 81.

[4] E. D. Bergmann and J. Klein, *J. Org. Chem.*, **23**, 512 (1958).

[5] W. Treibs and H. J. Klinkhammer, *Ber.*, **83**, 367 (1950).

[6] E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim. France*, **18**, 684 (1951).

[7] A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, **53**, 1668 (1951).

pellets) of the saturated and the unsaturated ketones VII (1605, 1650 cm.$^{-1}$), and VIII (1640 cm.$^{-1}$), and even less in the isomeric series (1603, 1650, and 1605, 1658 cm.$^{-1}$); this shows that the additional double bond in the central ring of VIII and IX does not contribute to the polarity of the ketonic group.[8]

The two heptafulvene ketones (VIII, IX) show a pronounced dependence of their carbonyl absorption on the solvent (see Experimental). As it is unlikely that this effect, which also appears in tropone, is a conformational one, it may indicate a change in polarity of the double bond as a function of interaction with the solvent.

The two ketones (VIII, IX) were treated both with benzyl- and *p*-chlorobenzylmagnesium chloride. The tertiary carbinols so obtained were dehydrated by esterification with boiling acetyl chloride and pyrolysis of the acetates.[9] The heptafulvenes (III, IV) could be purified by distillation *in vacuo* or recrystallization and column chromatography. They are mostly crystalline solids and undoubtedly not mixtures of stereoisomers. The dipole moments of the four heptafulvenes are summarized in Table I.

TABLE I

Compound	Dipole moment (D.)
III, R = C_6H_5	1.02
III, R = C_6H_4Cl-*p*	2.03
IV, R = C_6H_5	1.02
IV, R = C_6H_4Cl-*p*	1.71

In all cases, including that of the corresponding compounds II, the moments, for which we have redetermined (R = C_6H_5, 1.58; R = C_6H_4Cl-*p*, 2.05) comparison of the benzylidene and the *p*-chlorobenzylidene compounds, show that the direction of the moment of the semicyclic bond is from the ring outwards, as predicted. The moments are also larger than that recently calculated for the unsubstituted heptafulvene (I) (0.23).[10]

It should be noted that the four heptafulvenes (III, IV) can theoretically appear in *stereoisomeric* forms, although, generally speaking, *cis–trans* isomerism is infrequent in the fulvenes series. However, the dipole moment of the isomeric forms would be expected to be practically identical, as the polycyclic part of the molecule will not make a significant contribution to its dipole moment. The dipole moments thus cannot be used for assignment of configuration.

The ultraviolet spectra, on the other hand, have, unfortunately, not yielded the expected information; the spectra were completely featureless, showing an extinction coefficient of more than 10,000 until about 340 mμ. A similar observation has been made already for the tribenzoheptafulvene (IIa).[4]

Experimental

3-(1-Naphthylmethylene)phthalide (V) and the **2-naphthyl isomer** were prepared according to Bergmann[11]; λ_{max}^{KBr} 1653, 1754 and 1666, 1754 cm.$^{-1}$, respectively.

***o*-[β-(1-Naphthyl)ethyl]benzoic acid (VI).**—A mixture of 30 g. of 3-(1-naphthylmethylene)phthalide, 26 g. of red phosphorus, and 125 ml. of hydriodic acid was heated for 8 hr. at 160° with vigorous stirring. After cooling, the solid material was filtered and extracted with concentrated ammonia solution. The solution so obtained was first extracted with ether and then acidified giving 24 g. (77%) of VI, which formed white needles, m.p. 155°, after recrystallization from benzene.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.6; H, 5.8. Found: C, 82.7; H, 6.0.

8,9-Benzo-10,11-dihydro-7*H*-cyclohepta[*a*]naphthalen-7-one (VII).—When 20 g. of VI was heated at 100° with 600 g. of polyphosphoric acid for 6 hr., a red solution was obtained which was diluted with water and extracted with benzene and ether. After washing with sodium carbonate solution and evaporation, 15 g. (93%) of VII was obtained. It was recrystallized from 2-propanol and melted at 104°; λ_{max}^{EtOH} 263 (4.33), 292 (3.98), 344 mμ (log ε 3.28).

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.4; H, 5.4. Found: C, 88.3; H, 5.5.

8,9-Benzo-10(or 11)-bromo-10,11-dihydro-7*H*-cyclohepta[*a*]-naphthalen-7-one.—A mixture of 15 g. of N-bromosuccinimide, 100 ml. of carbon tetrachloride, and 0.1 g. of benzoyl peroxide was refluxed for 4 hr., filtered, and the solution concentrated. The bromo derivative melted at 144° dec.; λ_{max}^{EtOH} 267 (4.26), 300 (3.85), 336 mμ (log ε 3.23); ν_{max}^{KBr} 1640 cm.$^{-1}$.

8,9-Benzo-7*H*-cyclohepta[*a*]naphthalen-7-one (VIII).—The crude bromo ketone was refluxed for 45 min. with 80 ml. of pyridine; after cooling, cold hydrochloric acid was added in excess and the product extracted into benzene. Thus, 8.5 g. (58%) of VIII was obtained from benzene as needles, m.p. 146°; λ_{max}^{EtOH} 283 mμ (log ε 4.43); ν_{CO} 1605, 1639 (benzene), 1639 (carbon disulfide), 1610, 1637 (carbon tetrachloride), 1613, 1645 (chloroform), 1587, 1592 cm.$^{-1}$ (dioxane).

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.0; H, 4.7. Found: C, 89.1; H, 4.5.

8,9-Benzo-7-benzyl-7*H*-cyclohepta[*a*]naphthalen-7-ol.—The ketone VIII (14 g.) was added to a solution prepared from 2 g. of magnesium and 14 g. of benzyl chloride. The product obtained by refluxing the mixture for 3 hr. was decomposed with ice and ammonium chloride and worked up as usual; b.p. 250° (0.5 mm.); yield, 14.2 g. (98%). The ultraviolet spectrum showed no selective absorption, but a broad band from 290–330 mμ (log ε 4.18).

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.4; H, 5.7. Found: C, 89.6; H, 5.6.

7-Benzylidene-8,9-benzo-7*H*-cyclohepta[*a*]naphthalene (III, R = C_6H_5).—A mixture of 10 g. of the foregoing compound and 30 ml. of acetyl chloride was refluxed for 3 hr., and the crude acetate, isolated by distillation of the excess acetyl chloride *in vacuo*, was pyrolyzed by heating it for 30 min. at 220°. The hydrocarbon distilled at 248° (1 mm.), and the crystalline distillate was recrystallized from a mixture of benzene and petroleum ether; m.p. 165°; yield, 8 g. (83%).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.5; H, 5.5. Found: C, 94.5; H, 5.7.

Analogously, **7-(*p*-chlorobenzyl)-8,9-benzocyclohepta[*a*]naphthalen-7-ol** was prepared from 4 g. of VIII, 0.6 g. of magnesium, and 5 g. of *p*-chlorobenzyl chloride and crystallized from butanol; m.p. 150°; yield, 4.5 (95%); λ_{max}^{EtOH} 240 (4.45), 325 mμ (log ε 4.11).

Anal. Calcd. for $C_{26}H_{19}ClO$: C, 81.6; H, 5.0. Found: C, 81.0; H, 4.9.

7-(*p*-Chlorobenzylidene)-8,9-benzo-7*H*-cyclohepta[*a*]naphthalene (III, R = C_6H_4Cl-*p*).—Acetylation of 5 g. of the preceding tertiary alcohol and pyrolysis of the acetate gave 91% of the fulvene, which distilled at 275° (2 mm.) and crystallized from 2-propanol in colorless needles, m.p. 150–151°.

Anal. Calcd. for $C_{26}H_{17}Cl$: C, 85.6; H, 4.7. Found: C, 85.0; H, 4.8.

***o*-[β-(2-Naphthyl)ethyl]benzoic Acid (as VI).**—In the manner described, 93 g. of 3-(2-naphthylmethylene)phthalide, heated during 8 hr. at 180° with 80 g. of red phosphorus and 380 ml. of

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[8] For the infrared spectra of other cyclohepta-2,4-dien-1-ones and -2,4,6-trien-1-ones (tropones), see E. D. Bergmann, *et al.*, ref. 6; E. D. Bergmann and J. Klein, ref. 4; G. P. Scott and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 240 (1950); E. von Doering and C. F. Hiskey, *ibid.*, **74**, 5688 (1952); D. Elad and D. Ginsburg, *J. Chem. Soc.*, 471 (1954); Y. Ikegami, *Bull. Chem. Soc. Japan*, **35**, 967, 972 (1962); H. Goetz, E. Heilbronner, A. K. R. Katritzky, and R. A. Jones, *Helv. Chim. Acta*, **44**, 387 (1961) (these authors also give an assignment of the observed peaks).

[9] In other cases, the tertiary carbinols which are the congeners of heptafulvenes also have proven to be unexpectedly refractory to dehydration.

[10] A. Julg, *J. chim. phys.*, **59**, 759 (1962).

[11] E. D. Bergmann, *J. Org. Chem.*, **21**, 461 (1956).

concentrated hydriodic acid, gave 68 g. (72%) of a product, m.p. 148–149°, after recrystallization from a mixture of benzene and ligroin.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.6; H, 5.8. Found: C, 83.0; H, 5.9.

9,10-Benzo-7,8-dihydro-11*H*-cyclohepta[*a*]naphthalen-11-one (as VII).—From 90 g. of the foregoing acid and 2.5 kg. of polyphosphoric acid, 65 g. (77%) of the ketone was obtained, which distilled at 230° (1.4 mm.) and melted, after recrystallization from 2-propanol, at 110–111°; $\lambda_{\max}^{\text{EtOH}}$ 255 (4.18), 315 (3.52), 325 mμ (log ϵ 3.50).

Anal. Calcd for $C_{19}H_{14}O$: C, 88.4; H, 5.4. Found: C, 88.7; H, 5.7.

9,10-Benzo-7-(or 8)-bromo-7,8-dihydro-11*H*-cyclohepta[*a*]-naphthalen-11-one.—A mixture of 3.5 g. of the foregoing ketone, 5.3 g. of N-bromosuccinimide, 50 ml. of carbon tetrachloride, and 0.1 g. of benzoyl peroxide was refluxed for 2 hr. The filtered solution contained already the dehydrobromination product IX in crude form. The brominated ketone had separated together with the succinimide formed. The solid phase was extracted with water and dried. The residue (7 g.), m.p. 152° dec., was the pure bromo ketone; $\lambda_{\max}^{\text{EtOH}}$ 257 (4.19), 315 (3.42), 330 mμ (log ϵ 3.44); $\nu_{\max}^{\text{KBr}}$ 1658 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{13}BrO$: C, 67.6; H, 3.9. Found: C, 67.4; H, 3.9.

9,10-Benzo-11*H*-cyclohepta[*a*]naphthalen-11-one (IX).—The foregoing bromo ketone, together with the crude residue of the carbon tetrachloride solution, was refluxed for 30 min. with 40 ml. of pyridine and worked up as described for the isomer VIII. The product (4.5 g., 60%) was recrystallized from a mixture of benzene and ligroin and melted at 136–137°, $\lambda_{\max}^{\text{EtOH}}$ 279 mμ (log ϵ 4.23); ν_{CO} 1610, 1615 (doublet), 1639 (benzene), 1639 (shoulder), 1653 (carbon disulfide), 1613, 1634, 1645 (carbon tetrachloride), 1613, 1639 (chloroform), 1585, 1605 cm.$^{-1}$ (dioxane).

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.0; H, 4.7. Found: C, 88.7; H, 4.8.

Oxidation of IX (Proof of Structure).—During 4 hr. a current of ozone was passed at −80° through a solution of 2 g. of IX in 100 ml. of methylene chloride. A white precipitate appeared in the greenish solution. The solvent was removed *in vacuo* at room temperature and the resulting solid taken up in 100 ml. of water and heated in the water bath for 1 hr. The yellowish product so obtained was filtered off and dissolved in sodium hydrogen carbonate solution. The solution was extracted with ether and then acidified with hydrochloric acid. The product (dicarboxylic acid) so obtained was heated at 170–180° for 15 min., giving off carbon dioxide, and the still acidic residue recrystallized from aqueous methanol. The slightly yellowish crystals melted at 174–175° and gave the analytical figures required for a naphthoylbenzoic acid.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.3; H, 4.3. Found: C, 78.3; H, 4.3.

That the acid was *o*-(1-naphthoyl)benzoic acid, corresponding to formula IX, was proven by comparison (no depression of the melting point) with an authentic specimen.[12]

11-Benzyl-9,10-benzo-11*H*-cyclohepta[*a*]naphthalen-7-ol.—From 7 g. of IX, 1 g. of magnesium, and 7 g. of benzyl chloride, a yield of 7.2 g. (91%) was obtained; b.p. 250° (0.6 mm.); $\lambda_{\max}^{\text{EtOH}}$ 270 (4.38), 276 (4.36), 284 (4.37), 323 mμ (log ϵ 4.15).

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.4; H, 5.7. Found: C, 90.0; H, 5.9.

11-Benzylidene-9,10-benzo-11*H*-cyclohepta[*a*]naphthalene (IV, R = C_6H_5).—Dehydration as in the case of the isomer gave a 86% yield of the fulvene, b.p. 230° (0.4 mm.).

Anal. Calcd. for $C_{22}H_{18}$: C, 94.5; H, 5.5. Found: C, 94.2; H, 5.5.

11-(*p*-Chlorobenzyl)-9,10-benzo-11*H*-cyclohepta[*a*]naphthalen-7-ol.—From 6 g. of IX, 7 g. of *p*-chlorobenzyl chloride, and 0.9 g. of magnesium, 7 g. (98%) of the tertiary alcohol was obtained, from methanol as colorless needles, m.p. 156°; $\lambda_{\max}^{\text{EtOH}}$ 234 (4.28), 274 (3.85), 283 (3.86), 322 mμ (log ϵ 4.11).

Anal. Calcd. for $C_{26}H_{19}ClO$: C, 81.6; H, 5.0. Found: C, 81.2; H, 5.0.

11-(*p*-Chlorobenzylidene)-9,10-benzo-11*H*-cyclohepta[*a*]-naphthalene (IV, R = C_6H_4Cl-*p*).—Dehydration of the preceding product, as described before, gave a 94% yield of the fulvene, b.p. 255° (0.5 mm.); from 2-propanol as colorless crystals, m.p. 152–153°.

Anal. Calcd. for $C_{16}H_{17}Cl$: C, 85.6; H, 4.7. Found: C, 85.0; H, 4.7.

Dipole Moments.—The dipole moments were measured in benzene solution at 30°, using the method of Halverstadt and Kumler[13]; the probable error is ±0.03 D.

7-Benzylidene-8,9-benzo-7*H*-cyclohepta[*a*]naphthalene (III, R = C_6H_5)

ω	ϵ	v
0.0003339	2.2648	1.1512
.0058471	2.2683	1.1504
.011315	2.2735	1.1479
.017874	2.2757	1.1465

P_∞ = 123.54 cm.^{3}
MR = 102.40 cm.^{3}
u = 1.02 D.

7-(*p*-Chlorobenzylidene)-8,9-benzo-7*H*-cyclohepta[*a*]naphthalene (III, R = C_6H_4Cl-*p*)

ω	ϵ	v
0.0033847	2.2699	1.15059
.0068689	2.2799	1.14946
.010985	2.2913	1.14824
.018037	2.2940	1.14517

P_∞ = 195.55 cm.^{3}
MR = 112.40 cm.^{3}
μ = 1.03 D.

11-Benzylidene-9,10-benzo-11*H*-cyclohepta[*a*]naphthalene (IV, R = C_6H_5)

ω	ϵ	v
0.0033802	2.2650	1.1512
.0058951	2.2669	1.1502
.011344	2.2770	1.1486
.018072	2.2748	1.1458

P_∞ = 120.43 cm.^{3}
MR = 99.54 cm.^{3}
μ = 1.02 D.

11-(*p*-Chlorobenzylidene)-9,10-benzo-11*H*-cyclohepta[*a*]naphthalene (IV, R = C_6H_4Cl-*p*)

ω	ϵ	v
0.0034211	2.2691	1.15059
.0064696	2.2740	1.14916
.010979	2.2794	1.14722
.017105	2.2865	1.14561

P_∞ = 176.30 cm.^{3}
MR = 117.40 cm.^{3}
μ = 1.71 D.

1-Benzylidene-2,3,6,7-dibenzocyclohepta-2,4,6-triene (II, R = C_6H_5)

ω	ϵ	v
0.0036653	2.2667	1.14397
.0068552	2.2745	1.14307
.011202	2.2808	1.14165
.017677	2.2922	1.13959

P_∞ = 157.36 cm.^{3}
MR = 91.98 cm.^{3}
μ = 1.58 D.

1-(*p*-Chlorobenzylidene)-2,3,6,7-dibenzocyclohepta-2,4,6-triene (II, R = C_6H_4Cl-*p*)

ω	ϵ	v
0.0037440	2.27144	1.14725
.0060230	2.27526	1.14661
.011496	2.28337	1.14453
.018432	2.29768	1.14257

P_∞ = 184.33 cm.^{3}
MR = 99.91 cm.^{3}
μ = 2.05 D.

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[12] C. Weizmann, E. Bergmann, and F. Bergmann, *J. Chem. Soc.*, 1367 (1935).

[13] I. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).