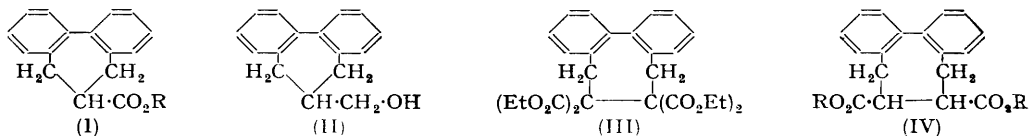


The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part V. 2:2'-Bridged Compounds with Seven- and Eight-membered Homocyclic Rings.*By G. H. BEAVEN, GWENDOLINE R. BIRD, D. MURIEL HALL, E. A. JOHNSON,
JOAN E. LADBURY, MARY S. LESSLIE, and E. E. TURNER.

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2:2'-Bisbromomethyldiphenyl has been condensed with the sodio-derivatives of ethyl malonate and ethyl ethane-1:1:2:2-tetracarboxylate. Hydrolysis of the esters produced, followed by decarboxylation, gave 3:4-5:6-dibenzocyclohepta-3:5-diene-1-carboxylic acid and two isomeric 4:5-6:7-dibenzocycloocta-4:6-diene-1:2-dicarboxylic acids respectively. The ultraviolet absorption spectra of the methyl esters of these acids are discussed in relation to their configurations. The condensation of the dibromide with ethyl propane-1:1:3:3-tetracarboxylate led to scission of the aliphatic ester and the formation of ethyl 3:4-5:6-dibenzocyclohepta-3:5-diene-1:1-dicarboxylate.

THE reaction between 2:2'-bisbromomethyldiphenyl and sodiomalonic ester produces ethyl 3:4-5:6-dibenzocyclohepta-3:5-diene-1:1-dicarboxylate (Kenner, *J.*, 1913, **103**, 613), from which 3:4-5:6-dibenzocyclohepta-3:5-diene-1-carboxylic acid (I; R = H) may be obtained. By the use of sodio-derivatives of other esters it was hoped to synthesise similar acids in which the 2:2'-bridge would form part of an eight- or nine-membered or even larger ring. In such compounds the increased size of the bridging ring may be expected to lead to greater twisting of the two benzene rings about the common axis with consequent further reduction in conjugation between them, detectable by changes in the ultraviolet absorption spectra.



We have succeeded in preparing the compounds containing an eight-membered bridging ring but not those with the larger rings.

3:4-5:6-Dibenzocyclohepta-3:5-diene-1-carboxylic acid (I; R = H) was prepared by Kenner's method. The absorption spectra of the acid, of its methyl ester (I; R = Me; Fig. 1) and of 1-hydroxymethyl-3:4-5:6-dibenzocyclohepta-3:5-diene (II) in 96% ethanol are all of the simple diphenyl type, with the conjugation band at the same wavelength as in diphenyl itself (249 m μ) but of slightly reduced intensity (*ca.* 15,000 instead of 17,000). The long-wave features in the spectra of these three compounds are barely discernible inflections; their apparent molecular extinctions are irrelevant because of heavy overlapping by the strong conjugation bands, and the actual contributions from the phenyl partial chromophores must be very small. The small reduction in conjugation compared with diphenyl is thus practically the same as that observed with the seven-membered bridged heterocyclic compound, 2:7-dihydro-3:4-5:6-dibenzoxepin (Part I; Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854).

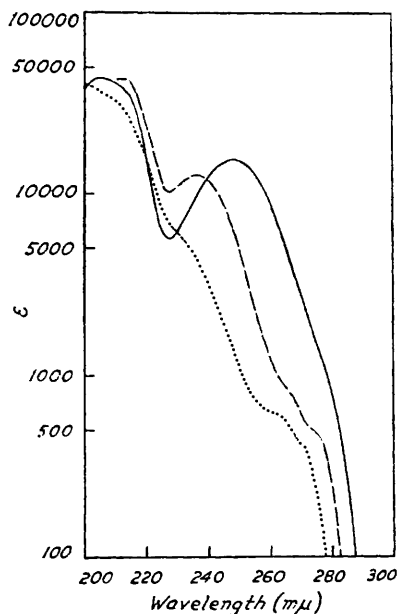
The angle between the ring planes in the 3:4-5:6-dibenzocyclohepta-3:5-diene structure according to a model is about 50°; direct calculation (using 1.54 Å for the C₍₁₎-C₍₂₎ and C₍₂₎-C₍₃₎ bonds and 1.40 Å for the C₍₃₎-C₍₄₎ bond) gives a value of 48.6° if the C₍₄₎-C₍₅₎ bond is 1.53 Å and 49.1° if the C₍₄₎-C₍₅₎ bond is 1.50 Å.

All attempts to effect the optical resolution of the acid (I; R = H) or the alcohol (II) failed (*cf.* Bell, *J.*, 1952, 1527). The brucine, quinine, and strychnine salts of the acid were

* Part IV, *J.*, 1954, 2552.

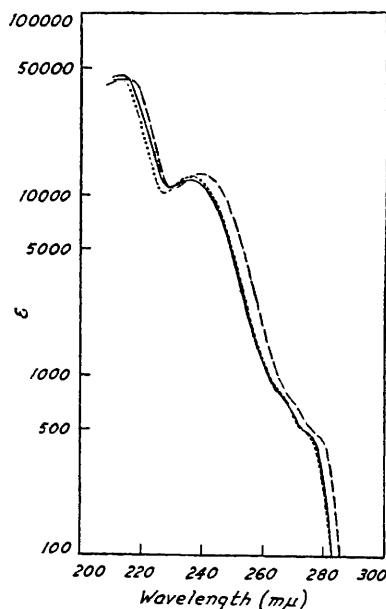
investigated in various solvents and also the (–)-menthyl and (–)-cholesteryl esters. The (–)-menthoxyacetate and the brucine salt of the hydrogen phthalate of the alcohol were studied. Decarboxylation of the dibrucine salt of 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1 : 1-dicarboxylic acid yielded optically inactive monocarboxylic acid. The quinine salt of (I) showed a rather unusual feature in that the quinine behaved as a diacidic base, even when the salt was prepared in ethanol starting with *equimolecular* proportions of acid and alkaloid. The (1 : 1)-salt was obtained from an acetone–light petroleum solution, but on

FIG. 1.



— Methyl 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1-carboxylate (I; R = Me).
 --- Methyl 4 : 5-6 : 7-dibenzocycloocta-4 : 6-diene-1 : 2-dicarboxylate (IV; R = Me), m. p. 139–141°.
 - - - 2 : 2'-Di-(2-methoxycarbonyl-*n*-propyl)-diphenyl.

FIG. 2.



--- Ethyl 4 : 5-6 : 7-dibenzocycloocta-4 : 6-diene-1 : 1 : 2 : 2-tetracarboxylate (III).
 — Methyl 4 : 5-6 : 7-dibenzocycloocta-4 : 6-diene-1 : 2-dicarboxylate (IV; R = Me), m. p. 126-5–128°.
 - - - Methyl 4 : 5-6 : 7-dibenzocycloocta-4 : 6-diene-1 : 2-dicarboxylate (IV; R = Me), m. p. 139–141°.

crystallisation from ethanol gave the (2 : 1)-salt together with a gel which was mainly quinine. The methyl ester (I; R = Me) was examined for unstable optical activity by dissolution in diethyl (+)-tartrate (Buchanan and Graham, *J.*, 1950, 500; Glazer, Harris, and Turner, *ibid.*, p. 1753) with negative results. Further, the acid itself failed to undergo first-order asymmetric transformation in the presence of brucine in chloroform solution.

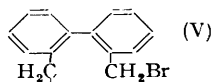
Kenner (*loc. cit.*) condensed 2 : 2'-bisbromomethyldiphenyl with ethyl ethane-1 : 1 : 2 : 2-tetracarboxylate in the presence of sodium ethoxide in ethanol at 120–140° under pressure for 5 hours and obtained a crystalline ester, m. p. 108.5°, with the correct analysis for the expected product (III) but with a low molecular weight as determined cryoscopically in benzene solution. We have obtained the same compound by adding the dibromide in ethereal solution to the sodio-ester in ethanol and then distilling off the ether during 3 hours; the solution then had a "neutral" reaction. The molecular weight of the ester as observed in undried benzene was a little low but as determined ebullioscopically in benzene solution by Menzies and Wright's method (*J. Amer. Chem. Soc.*, 1921, **43**, 2314) was correct.

The absorption spectrum of the ester (III) (Fig. 2) is very similar to the spectra of the corresponding dicarboxylic esters (IV; R = Me) discussed below, except for a general small shift (2–4 $m\mu$) to longer wavelengths.

Alkaline hydrolysis in 2-ethoxyethanol was accompanied by decarboxylation, giving a dicarboxylic acid (IV; R = H), m. p. ca. 235° (decomp.). When this was heated at 250—260° it passed partly into an anhydride, which on dissolution in potassium hydroxide, followed by acidification with cold acid, gave a second dicarboxylic acid, obtained as a partial hydrate, m. p. ca. 202° (decomp.). The two acids gave rise to two series of esters, those from the second acid having the higher melting points. It was not found possible to obtain a pure anhydride from the first acid. The most probable explanation of the two series of compounds is that they are *cis* and *trans* isomers, although the possibility of additional diastereoisomerism arising from the twisted ring system together with the asymmetric carbon atoms cannot be ruled out.

The ultraviolet absorption spectra of the two isomeric methyl esters (IV; R = Me) are virtually identical (Fig. 2); the observed differences are, however, believed to be real. The spectra indicate that conjugation between the two benzene rings of the diphenyl skeleton in (IV) is considerably reduced in comparison with (I). The conjugation band is shifted to a shorter wavelength (236.5 instead of 248.5 m μ) and is reduced in intensity; and as a result of the short-wave shift the minimum at ca. 228 m μ is raised very considerably from $\epsilon_{\min.}$ ca. 6000 to ca. 10,500. Further evidence for reduced conjugation is the appearance of long-wave inflections, which are much better resolved than the scarcely perceptible inflection shown by (I). The extinction coefficients at the long-wave inflections in (I) and (IV) cannot be taken as indications of the relative contributions of the phenyl partial chromophores in the two sets of compounds, as there is severe overlapping in both cases by the conjugation bands. Nevertheless, considerable conjugation between the two benzene rings still persists in spite of the large angle between them. From models this appears to be of the order of 60—65°. It is also possible to construct models in which greater overcrowding of the bridging ring and its substituents occurs and in this configuration the angle between the benzene rings is of the order of 75—80°. Models cannot give accurate information about the interconvertibility of these two configurations, but for steric reasons the second one is not likely to be a preferred configuration; and the spectral evidence of remaining conjugation favours the configuration with the smaller angle. The contrast between non-coplanar bridged diphenyls and those with non-bridging 2 : 2'-substituents is striking. In the latter, unless the 2 : 2'-substituents are very small (*e.g.*, fluorine, cf. Part VI) conjugation is very greatly reduced and the long-wave features are much more evident (cf. 2 : 2'-ditolyl, Part III, Beaven, Hall, Leslie, Turner, and Bird, *J.*, 1954, 131), even though transient coplanarity (in the "*trans*" position) can undoubtedly be achieved.

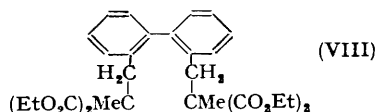
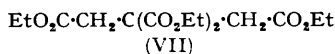
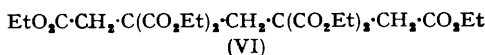
The interaction of 2 : 2'-bisbromomethyldiphenyl and ethyl propane-1 : 1 : 3 : 3-tetracarboxylate in the presence of sodium ethoxide failed to give the expected compound with a nine-membered bridging ring. Instead, fission of the carbon chain of the ester occurred and ethyl 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1 : 1-dicarboxylate was produced in about 60% yield. Hydrolysis and decarboxylation led to 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1-carboxylic acid (I; R = H), identified by mixed melting points, the absorption spectrum, and the molecular weight of its methyl ester. It seems likely that initially a singly charged anion of the ester is produced and reacts normally with one bromomethyl



(EtO₂C)₂C ^{α} -CH₂- ^{γ} CH(CO₂Et)₂

group, giving (V). In the second stage the other bromomethyl group is attacked by the α -carbon atom rather than the γ -carbon atom, even though the latter can acquire a negative charge (in the presence of ethoxide ions). Such behaviour by this ester is not unknown. Guthzeit and Engelmann (*J. prakt. Chem.*, 1902, 66, 104) found that it reacted with two molecules of ethyl bromoacetate in the presence of sodium ethoxide to give a mixture of the normal product, ethyl pentane-1 : 2 : 2 : 4 : 4 : 5-hexacarboxylate (VI) (attack in stage 2 by the γ -carbon atom), and ethyl propane-1 : 2 : 2 : 3-tetracarboxylate (VII) (attack in stage 2 by the α -carbon atom), the proportions varying with the experimental conditions and the yields being rather low. In the case of compound (V) attack by the α -carbon atom is strongly favoured sterically and although evidence of the product of attack by the γ -carbon atom was specifically looked for it was not obtained.

The strong tendency for the formation of the seven-membered ring is further shown by Kenner's observation (*loc. cit.*) that in the condensation between the dibromide and sodio-malonic ester, the use of two molecular proportions of malonic ester still leads to the same



cyclic product; whereas we find that with two molecular proportions of ethyl methylmalonate normal interaction occurs, giving 2 : 2'-di-(2 : 2-diethoxycarbonyl-*n*-propyl)diphenyl (VIII), and thence, by hydrolysis and decarboxylation, 2 : 2'-di-(2-carboxy-*n*-propyl)diphenyl. The spectrum of the dimethyl ester of this acid (Fig. 1) has the characteristics expected for an unbridged 2 : 2'-dialkyldiphenyl.

EXPERIMENTAL

3 : 4-5 : 6-Dibenzocyclohepta-3 : 5-diene-1-carboxylic acid, m. p. 161—162°, was prepared by Kenner's method (*loc. cit.*) from 2 : 2'-bisbromomethyldiphenyl (Hall, Leslie, and Turner, *J.*, 1950, 711) *via* 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1 : 1-dicarboxylic acid, m. p. ca. 218° (decomp.). The methyl ester had m. p. 46—47°.

Attempted Resolution.—(a) *Quinine salt.* The neutral salt was made by dissolving the acid (2.4 g., 2 mols.) and quinine dihydrate (1.8 g., 1 mol.) in ethanol (20 c.c.). The salt (3.1 g.) which separated was air-dried; it had $[\alpha]_{5791} - 69.7^\circ$, $[\alpha]_{5461} - 80.9^\circ$ (*c.* 2.699 in CHCl_3) (Found : C, 76.5; H, 7.1. $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot 2\text{C}_{16}\text{H}_{14}\text{O}_2 \cdot \text{C}_2\text{H}_6\text{O}$ requires C, 76.6; H, 6.9%). An identical salt ($[\alpha]_{5791} - 69.6^\circ$, $[\alpha]_{5461} - 80.7^\circ$) was obtained by dissolving equimolecular amounts of acid and quinine dihydrate in ethanol. In this case evaporation of the solvent from the mother-liquor gave a glass which was mainly quinine. The basic salt was obtained by dissolving equimolecular amounts of the acid and anhydrous quinine in acetone and adding light petroleum (b. p. 60—80°). This salt had $[\alpha]_{5791} - 89.8^\circ$, $[\alpha]_{5461} - 104.2^\circ$ (in CHCl_3); a chloroform solution made up to contain equimolecular amounts of the acid and quinine had $[\alpha]_{5791} - 89.0^\circ$, $[\alpha]_{5461} - 102.8^\circ$. Crystallisation of this salt from ethanol gave the neutral salt, $[\alpha]_{5791} - 69.5^\circ$, $[\alpha]_{5461} - 81.0^\circ$, and a gel which was mainly quinine.

(b) *Cholesteryl ester.* The acid chloride was prepared by using thionyl chloride and was obtained as a solid, m. p. 72—74° after crystallisation from light petroleum (b. p. 40—60°) (cf. Kenner, *loc. cit.*). The chloride (8 g.), dissolved in benzene (20 c.c.), was added to cholesterol (10.8 g.), dissolved in pyridine (50 c.c.), and the mixture warmed to 50°. After 3 hr. dilute hydrochloric acid was added; the benzene solution was separated and washed, and the solvent removed. The crude ester (14.5 g.) was crystallised from acetone and had m. p. 105—107°, $[\alpha]_{5791} - 20.6^\circ$, $[\alpha]_{5461} - 23.9^\circ$ (*c.* 2.426 in CHCl_3) (Found : C, 85.1; H, 9.95. $\text{C}_{43}\text{H}_{58}\text{O}_2$ requires C, 85.1; H, 9.6%). The specific rotation was unchanged by further recrystallisation.

1-Hydroxymethyl-3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene (II).—The alcohol was prepared by the reduction of methyl 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1-carboxylate with lithium aluminium hydride in ethereal solution. It crystallised from benzene-light petroleum (b. p. 60—80°) in needles, m. p. 131.5° (Found : C, 85.5; H, 7.2. $\text{C}_{16}\text{H}_{16}\text{O}$ requires C, 85.7; H, 7.1%). The hydrogen phthalate, crystallised from aqueous acetic acid, had m. p. 145° (Found : C, 77.1; H, 5.4. $\text{C}_{24}\text{H}_{20}\text{O}_4$ requires C, 77.4; H, 5.4%). A brucine salt of the hydrogen phthalate was made but its specific rotation was unaltered by repeated crystallisation, and decomposition gave the inactive hydrogen phthalate. The (–)-menthoxyacetate was made by the usual method in pyridine solution. It crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 62—63° (Found : C, 80.2; H, 8.3. $\text{C}_{28}\text{H}_{36}\text{O}_3$ requires C, 80.0; H, 8.6%). The specific rotation varied slightly on recrystallisation but no clear separation into two esters occurred.

Ethyl 4 : 5-6 : 7-Dibenzocycloocta-4 : 6-diene-1 : 1 : 2 : 2-tetracarboxylate.—Sodium (4.1 g., 2 atom-equivs.) was dissolved in absolute ethanol (85 c.c.), and ethyl ethane-1 : 1 : 2 : 2-tetracarboxylate (28 g., 1 mol.) added (as solid) with stirring, followed immediately by the dibromide (30 g., 1 mol.) in ethereal solution (250 c.c.). The mixture was heated under reflux for 1 hr. and then the ether distilled off during 3 hr. The solution then had a neutral reaction. Water was added and the solid ester so obtained was washed with light petroleum and crystallised from *n*-hexane, giving 23 g. (52%), m. p. 107—109°. Recrystallisation raised the m. p. to 108—109.5°

[Found: C, 67.7; H, 6.2%; *M* (cryoscopic in undried benzene) 455, (in cyclohexane) 456; (ebullioscopic in benzene) 502, 501. Calc. for $C_{28}H_{32}O_8$: C, 67.7; H, 6.5%; *M*, 496].

4 : 5-6 : 7-Dibenzocycloocta-4 : 6-diene-1 : 2-dicarboxylic Acids.—Hydrolysis of the tetraethyl ester. (a) The ester was boiled under reflux with ethanolic potassium hydroxide for 6 hr. and water then added. About half the ester was recovered unchanged. This was then treated with ethanolic potassium hydroxide for another 15 hr. The acid so obtained (from both parts of the hydrolysis) was crystallised from aqueous ethanol and had m. p. ca. 230° (decomp.).

(b) The ester was boiled under reflux for 6 hr. with potassium hydroxide dissolved in 2-ethoxyethanol containing a little water. A large volume of water was added, the solution extracted with ether, and hydrochloric acid added. The acid was crystallised from aqueous alcohol and had m. p. ca. 235° (decomp.). Analysis showed it to be the dicarboxylic acid (Found: C, 72.6; H, 5.6. $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.4%). The yield was 81%.

Some of this acid (6.0 g.) was heated at 250° and it decomposed with loss of water (it was at this time supposed to be the tetracarboxylic acid). The residue was dissolved in hot ethanol and the solution deposited an anhydride (1.65 g.) which, after recrystallisation from cyclohexane, had m. p. 173—174° (Found: C, 77.5; H, 5.2. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.1%).

The anhydride was dissolved in hot aqueous potassium hydroxide and the acid precipitated from the cooled solution. This acid crystallised from aqueous ethanol and had m. p. ca. 202° (decomp.). It appeared to be partially (and variably) hydrated (Found: C, 71.3, 72.4, 70.8; H, 6.2, 5.7, 5.5. $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.4. $C_{18}H_{16}O_4 \cdot H_2O$ requires C, 68.8; H, 5.8%). It could be reconverted into the anhydride by the action of boiling acetic anhydride. The dimethyl ester was prepared from the anhydride and crystallised from methanol in long prisms, m. p. 139—141° (Found: C, 74.2; H, 6.4. $C_{20}H_{20}O_4$ requires C, 74.05; H, 6.2%). The diethyl ester, crystallised from ethanol, had m. p. 77—78.5° (Found: C, 75.2; H, 7.0. $C_{22}H_{24}O_4$ requires C, 75.0; H, 6.9%).

Esters were prepared from the isomeric acid, m. p. 235° (decomp.). The dimethyl ester had m. p. 126.5—128° (Found: C, 74.0; H, 6.4%). The diethyl ester had m. p. 58.5—60° (Found: C, 74.9; H, 7.05%). Attempts to prepare the anhydride of this acid were unsuccessful.

The ethanolic mother-liquor, after separation of the anhydride, was concentrated, but no more solid was obtained, presumably owing to reaction of the anhydride with ethanol to give the half-ester. The ethanolic solution was therefore heated with alcoholic potassium hydroxide, and acid (3.4 g.) recovered from it. This was a mixture of the two acids and, although separation was difficult, a little of each acid was isolated from it.

Reaction of 2 : 2'-Bisbromomethylphenyl with Ethyl Propane-1 : 1 : 3 : 3-tetracarboxylate.—The ester (*Org. Synth.*, Coll. Vol. I, 2nd edn., p. 290) was fractionated four times under reduced pressure. Sodium (3.45 g., 2 atom-equivs.) was dissolved in absolute ethanol (60 c.c.), and the ester (24.9 g., 1 mol.) added with stirring, followed by the dibromide (25.5 g., 1 mol.), which had been finely ground and dissolved in the minimum amount of dry ether (ca. 220 c.c.). Immediate separation of sodium bromide occurred. The ether was removed by distillation during 2 hr. and the mixture then boiled under reflux for another hour. It then had a neutral reaction to litmus. Water was added and the oil extracted with ether, dried, and twice distilled under reduced pressure. The main fraction (15.3 g., 60%) had b. p. 166—170°/1 mm. In addition a small fraction (2.6 g.) with b. p. <100°/1 mm. was obtained and also a fraction (4.2 g.) distilling over a considerable range from which, after hydrolysis, a little more acid was subsequently isolated. Distillation was stopped when the residue in the distilling flask began to decompose. The bromide ion in the aqueous solution was estimated gravimetrically and found to be 96.2% of the total bromine originally present.

The ester was hydrolysed with boiling ethanolic potassium hydroxide, and the resultant acid crystallised from aqueous ethanol. It had m. p. ca. 218° (decomp.), not depressed on admixture with 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1 : 1-dicarboxylic acid (Found: C, 72.6; H, 5.2. Calc. for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0%). The yield of crystallised material was 9.65 g. (46% from the dibromide).

The acid was decarboxylated by heating it at 230°. The product crystallised from ethanol in rods, m. p. 161—162° (Found: C, 80.6; H, 6.1%; *M*, 490; equiv., 247. Calc. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.9%; *M*, 238; equiv., 238). The acid is thus dimeric in benzene. A mixed m. p. with 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1-carboxylic acid was 161—162°. The methyl ester had m. p. 46—47° [Found: C, 80.9; H, 6.5%; *M* (in cyclohexane), 244. Calc. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4%; *M*, 252]. Light absorption for the acid in 96% ethanol: λ_{max} , 249 m μ (ϵ 15,300), λ_{min} , 228 m μ (ϵ 5550); cf. data in Table.

In another preparation on the same scale the crude ester was hydrolysed without initial

distillation. The crude acid so obtained was difficult to purify. Oily (acidic) impurities were removed by treatment with a little boiling benzene (in which the required acid is practically insoluble) and 10.8 g. (51%) of good-quality dicarboxylic acid were eventually obtained.

In another preparation only half the calculated quantity of ethyl propane-1 : 1 : 3 : 3-tetracarboxylate was used. The crude ester was hydrolysed and eventually a 30% yield (based on dibromide used) of nearly pure dicarboxylic acid was obtained. But 92.5% of the total bromine was present as bromide ions at the end of the reaction.

2 : 2'-Di-(2 : 2-dithoxycarbonyl-*n*-propyl)diphenyl (VIII).—Sodium (2.8 g., 2 atom-equivs.) was dissolved in ethanol (150 c.c.) and ethyl methylmalonate (Cox and McElvain, *Org. Synth.*, Coll. Vol. II, pp. 272, 279) (20.5 g., 2 mols.) added, immediately followed by powdered 2 : 2'-bis-bromomethyldiphenyl (20 g., 1 mol.). Immediate separation of sodium bromide occurred. The mixture was heated under reflux for 3 hr. Some ethanol was distilled off; the residue was poured into water and the solid ester filtered off. 2 : 2'-Di-(2 : 2-dithoxycarbonyl-*n*-propyl)-diphenyl crystallised from ethanol in needles, m. p. 107° (25 g., 81%) (Found : C, 68.5; H, 7.3. $C_{30}H_{38}O_8$ requires C, 68.4; H, 7.3%).

2 : 2'-Di-(2-carboxy-*n*-propyl)diphenyl.—The above ester was hydrolysed by boiling with ethanolic potassium hydroxide, and the resultant tetracarboxylic acid, m. p. 200° (decomp.), heated at 220° for 30 min. The residue was dissolved in 10% aqueous sodium carbonate, and the extract, after being washed with ether, was acidified. The precipitate was washed with light petroleum (b. p. 60—80°). 2 : 2'-Di-(2-carboxy-*n*-propyl)diphenyl crystallised from benzene in prisms, m. p. 155—158° with some previous softening, and was presumably a mixture of diastereoisomers (Found : C, 73.8; H, 6.7. $C_{20}H_{22}O_4$ requires C, 73.6; H, 6.8%) (yield, 11.6 g., 60% from the dibromide). The diethyl ester had b. p. 194—196°/3 mm., n_D^{25} 1.5248 (Found : C, 75.3; H, 7.6. $C_{24}H_{30}O_4$ requires C, 75.3; H, 7.9%). The dimethyl ester crystallised from aqueous ethanol in rectangular plates, m. p. 68° (Found : C, 74.5; H, 7.7. $C_{22}H_{26}O_4$ requires C, 74.5; H, 7.4%).

Absorption Spectra.—Spectra were measured on an automatic recording spectrophotometer (cf. Part I, *loc. cit.*) and on Unicam SP. 500 manual instruments. Fine-structure features were

Ultraviolet absorption spectra.

Compound	Short-wave band				Conjugation band		Long-wave features	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{min.}$	$\epsilon_{min.}$	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{inf.}$	$\epsilon_{inf.}$
3 : 4-5 : 6-Dibenzocyclohepta-3 : 5-diene-1-carboxylic acid (I; R = H)	205	43,000	228	5770	249	15,300	(ca. 274)	ca. 1750
Methyl 3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene-1-carboxylate (I; R = Me)	207.5	42,500	227.5	5700	248.5	15,500	(ca. 274)	ca. 1700
1-Hydroxymethyl-3 : 4-5 : 6-dibenzocyclohepta-3 : 5-diene (II)	205.5	43,000	227.5	5400	248.5	15,400	(ca. 269) (ca. 277)	ca. 3200 ca. 1500
Ethyl 4 : 5-6 : 7-dibenzocycloocta-4 : 6-diene-1 : 1 : 2 : 2-tetracarboxylate (III)	215	43,400	230.5	10,900	239.5	13,100	(269) (278)	765 475
Methyl 4 : 5-6 : 7-dibenzocycloocta-4 : 6-diene-1 : 2-dicarboxylate (IV; R = Me), m. p. 139—141°	212.5	43,300	227.5	10,250	236.5	12,700	(266) (274)	810 492
Methyl 4 : 5-6 : 7-dibenzocycloocta-4 : 6-diene-1 : 2-dicarboxylate (IV; R = Me), m. p. 126.5—128°	213	45,600	229	10,950	236.5	12,150	(267) (275)	760 480
2 : 2'-Di-(2-methoxycarbonyl- <i>n</i> -propyl)diphenyl	(ca. 206?)	36,000	—	—	(230)	6050	(261) (270.5)	615 405

Solvent, 96% ethanol; wavelengths ($\mu\mu$) in parentheses denote inflections.

confirmed by the moving-plate logarithmic cam method (Holiday, *J. Sci. Inst.*, 1937, 14, 166) but the wavelengths given in the Table for inflections are the values obtained by direct examination of large-scale plots.

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