(13) J. W. ApSimon and H. Bierbeck, *J. Chem. Soc., Chem. Commun.*, 172 (1972).
(14) We have observed repeatedly that the algorithm auto-assignment[23] finds an L-S complex which has the smallest possible *R* factor for that data set under investigation. In the event that we auto-assign all resonances in a molecule whose resonances were independently identified, we recover the correct L-S array. In one or two cases we find a second L-S array, with some assignments differing, which was characterized by a smaller *R* factor. In general, we find that it is an excellent screening device since poor structures give large minimum *R* values and these can be rejected with confidence.
(15) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964, pp 157–162.
(16) We thank Dr. Guilford Jones, II, for details of this procedure.
(17) Prepared in 21% overall yield as described by P. K. Freeman, D. M. Balls, and D. J. Brown, *J. Org. Chem.*, **33**, 2211 (1968).
(18) Methods tried included a number of preparative GLC columns, washing ethereal solutions with aqueous silver nitrate or sodium bisulfite, and column chromatography on silver nitrate–silica gel.
(19) Procedure of C. K. Steinhardt as described by L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 584.
(20) A. Bowers, T. G. Halsall, E. R. H. Jones, and J. A. Lemin, *J. Chem. Soc.*, 2548 (1953).
(21) These two markers are shifted upfield due to a bulk susceptibility effect, but they maintain the same 7.26-ppm relationship and thus serve as reference points for the measurement of all the signals. This is useful, especially since Eu(fod)$_3$ itself has a strong absorption near tetramethylsilane.
(22) The instrument often needs retuning for each new doping ratio. A delay of several minutes between placing the doped sample in the probe and running the spectrum minimizes the retuning problem.
(23) The program PDIGM includes the autoassign algorithm. Copies of the program are available on request from R.E.D. or M.R.W.

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# Synthesis and Properties of Some Heterocirculenes[1]

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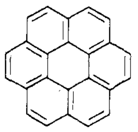
*Received December 27, 1974*

The synthesis of some heterocirculenes is reported. Based on a model study, we recognize two classes of circulenes, namely planar and nonplanar ones. Depending on the ratio of the outer and inner radii, bowl-shaped and corrugated nonplanar circulenes may exist. Attempts to prove that [7]-heterocirculenes belonged to the corrugated type of circulenes failed. The spectral characteristics of heterocirculenes are reported in detail.

**Coronene and Corannulene.** Coronene (1) is unique in the family of polycyclic aromatic compounds.[2] It has been of interest for many years not only because of its symmetric graphite-like structure but also because its synthesis continues to present a challenge to the ingenuity of the organic chemist. Scholl and Meyer announced in 1932 the first synthesis of **1**.[3a] Since then others have reported improved syntheses of **1**.[3bc] The high symmetry of the coronene molecule is of great value in the interpretation of spectroscopic results and their mathematical treatment. Coronene is an alternant hydrocarbon. According to the Hückel approximation there is no net charge on any atom in the system and the energy levels are symmetrically placed about the value of the $\alpha$ integral.[4] A complete determination of the coronene structure has been obtained by X-ray analysis.[5] It is a completely flat molecule. The carbon–carbon length varies in different parts of the molecule. The central ring and the "spokes" connecting it to the outer edges have bond lengths of 1.43 Å. The outer bonds are of two types measuring 1.41 and 1.38 Å. The planarity of coronene—and its many benzoid homologs—is an obvious consequence of the angular fusion of six benzene rings in the manner indicated (see **1**). When the number of aromatic rings—angularly annulated to form a "coronene"—deviates from six, the possibility of nonplanarity arises. A classical example of this type of molecules is corannulene (**2**), first prepared and studied by Barth and Lawton.[6] It has attracted much interest because despite its coronene-like structure it differs from the latter in two essential features. (a) Corannulene is a nonplanar, highly strained molecule. X-Ray analysis[6] demonstrates that it has a bowl-like shape (Figure 1). (b) Corannulene is a nonalternant hydrocarbon.[4] According to the Hückel theory, the electronic charge on each carbon atom differs in the ground state from one. An attractive way to accommodate this charge separation is found in structure **3**, in which two concentric annulene systems are formed. Both the cyclopentadienyl anion as well as the cyclopentadecaheptaenyl cation obey the well-known Hückel $4n + 2$ rule. SCF-MO calculations carried out by Gleicher[7] support the idea that **3** contributes to the stability of the ground state. However, no experimental data have been presented which substantiate any contribution from **3**.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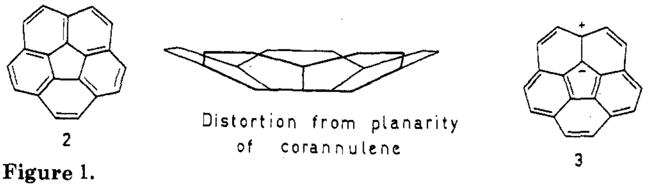


**Figure 1.**

**Results of a Model Study.** The structural differences between 1 and 2 (planarity vs. nonplanarity) can be made clearer by the following considerations. It is assumed that there are two circles of fixed diameter both of which are (within moderate limits) flexible. These circles (radii $r1$ and $r2$, $r1 < r2$) are connected by spokes of a constant length $a$ (Figure 2).

The optimal geometry will be determined by the following factors.

(a) If $r1 + a = r2$ then both circles will lie in a common plane (Figure 2a), as in coronene (1).

(b) If $r1 + a > r2$ then a likely geometry is one in which

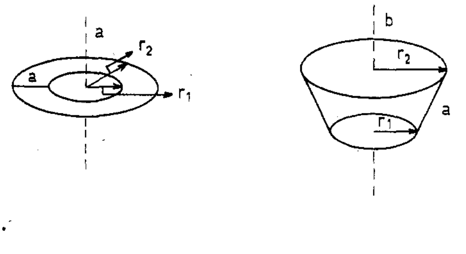
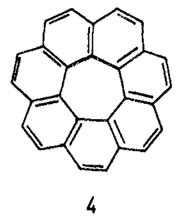


**Figure 2.**

the two circles lie in parallel planes (Figure 2b), as in corannulene (2).

(c) If $r1 + a < r2$ then the "extra" diameter of the outer circle is taken up by forming an unending wave; in other words, the system becomes corrugated. Molecular models indicate that this can be exemplified by the conformation of the hitherto unknown compound **4** (Figure 3).



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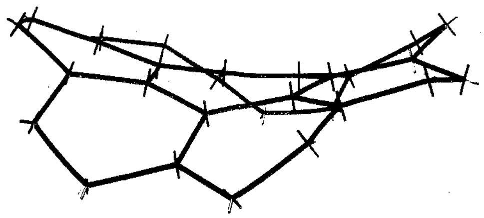
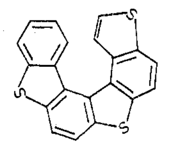


**Figure 3.**

$r1$ and $r2$ can be varied endlessly. Consequently the number of possible molecules which conform to these restraints is almost unlimited. Since the term "coronene" is firmly established to one compound and because of their circular arrangement of aromatic rings, it is proposed that this class of molecules be called *circulenes*.[8] A [$m$]-circulene is then a circulene constructed out of $m$ aromatic rings. A circulene in which one or more aromatic rings are replaced by a heterocyclic ring will be called a heterocirculene.

**Heterocirculenes.** A study of the preparation of heterohelicenes was started around 1966 by Groen and Wynberg.[10,11] By 1971, the synthetic pathways leading to heterohelicenes were improved in such a way that these helicenes were "available" for a further study.

Among the many points of interest was the question of transannular effects. This led to the preparation of **6**, a compound in which the two helical termini of **5** are connected by a $\sigma$ bond. Molecules like **6** were called dehydrohelicenes.[12] This compound was of particular interest to us because in its structure a great deal of that of the [7]-heterocirculene **7** was realized. Moreover, simple models suggested that this circulene **7** could have the nonplanar corrugated structure proposed above. (The limits of bond length adjustments which might keep a "corrugated" circulene planar are not known, of course.) One other early example of a heterocirculene exists. Erdtman and Högberg[13] cyclized a number of quinones under the influence of acids. The [8]-heterocirculene **8** is obtained in low yield when $p$-benzoquinone is treated with a mixture of sulfuric acid, acetic acid, and water (Figure 4). The authors expect **8** to be planar or nearly planar. The structure of **8** has not yet been determined by X-ray analysis.



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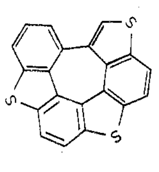

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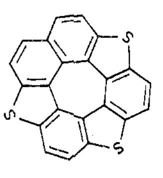

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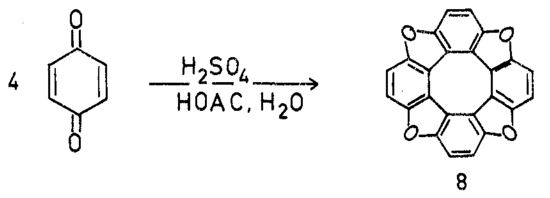


**Figure 4.**

**The Preparation of Heterocirculenes.** Patterned after the Diels–Alder addition of maleic anhydride to perylene,[3b] we found that when the dehydrohelicene **6** was allowed to react with maleic anhydride in the presence of chloranil as

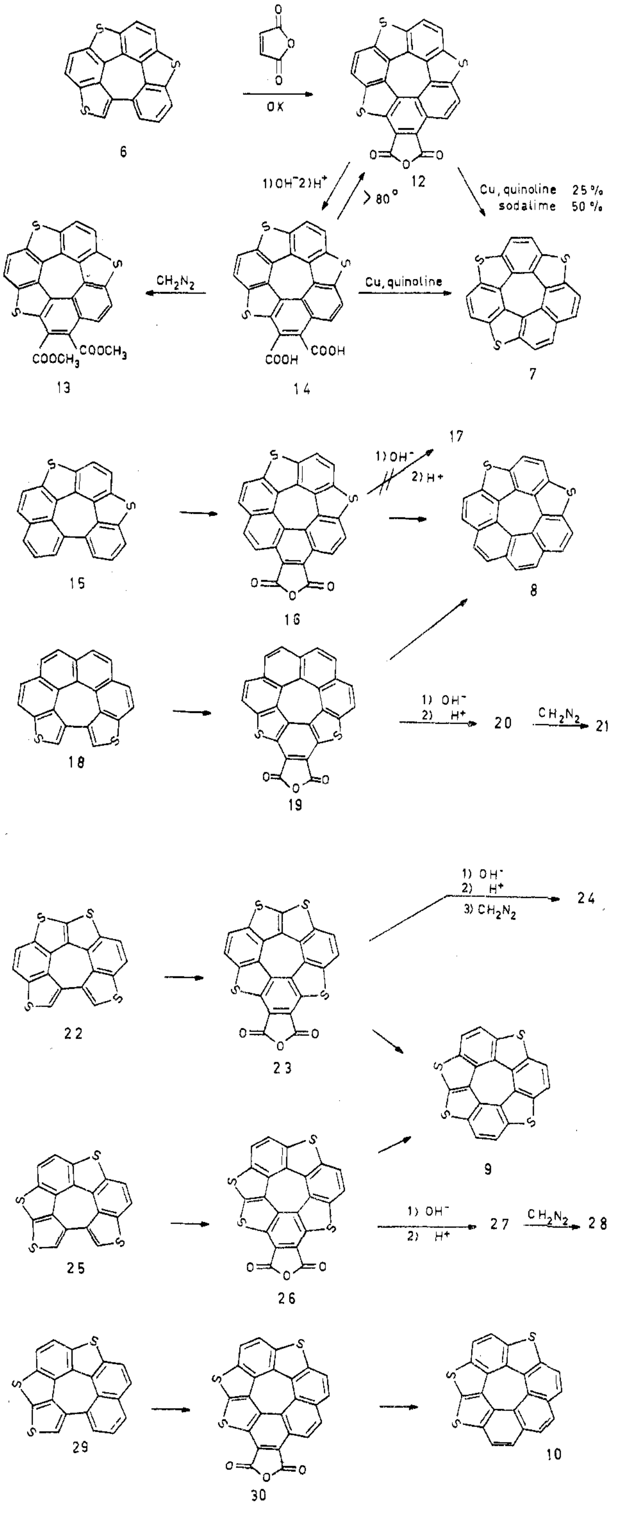


**Figure 5.**

oxidizing agent, the red anhydride **12** (mp above 400°) was obtained in 65% yield (Figure 5). When the reaction was carried out without an oxidizing agent no reaction was observed and the starting materials were recovered completely. Chloranil was superior to sulfur, nitrobenzene, or oxygen as an oxidizing agent. The anhydride **12** was only slightly soluble in nitrobenzene and quinoline whereas it was almost completely insoluble in common organic solvents. From **12** no NMR, uv, and MS could be obtained. Its ir spectrum showed the principal absorptions at 1825 and 1722 cm$^{-1}$, absorptions characteristic for the anhydride moiety.

The anhydrides **16**, **19**, **23**, **26**, and **30** were prepared by the same method and are shown in Figure 5.

In Diels–Alder reactions of this type maleic anhydride has some distinct advantages. It is a reactive but stable dienophile which can withstand high temperatures for long reaction periods. This in contradistinction to dienophiles like dicyanoacetylene, which is known to polymerize at higher temperatures.[14] An additional important factor is the insolubility of the obtained anhydrides, which makes them easy to isolate from the reaction mixtures. When instead of maleic anhydride, dicyanoacetylene or dimethyl acetylenedicarboxylate were used as dienophiles, very complex reaction mixtures were obtained from which no definite products could be isolated. With acrylonitrile no reaction was observed. Somewhat better results were obtained when methyl propiolate was used. The addition product **31** was obtained in 34% yield when **18** was allowed to react with methyl propiolate at 130° for 48 hr (Figure 6). When **31** was hydrolyzed an acid **32** was obtained which upon decarboxylation gave the heterocirculene **8** in 40% yield.

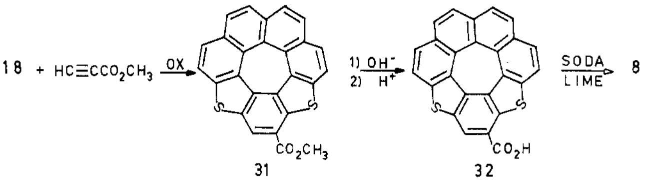
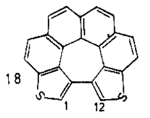
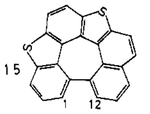
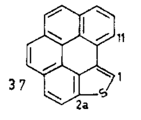


**Figure 6.**

**The Para-Localization Energies.**[15,16] The yields in which the anhydrides are formed from the corresponding dehydrohelicenes vary from 17 to 70%. This indicates that the dehydrohelicenes differ from one another in their reactivity toward Diels–Alder additions. For the two isomeric dehydrohelicenes **15** and **18** we calculated the para-localization energies for the positions indicated in Table I using HMO methods.[4,17] The results are in agreement with the experimental data.

**Table I**

| Compd | Diels–Alder yield, % | Para-localization energies (Dewar) in β units | Positions | Para-localization energies (Brown) in β units |
|---|---|---|---|---|
| 18  | 60 | 3.712 | 1.12 | 3.120 |
| 15  | 17 | 4.624 | 1.12 | 4.140 |
| 37  |  | 4.053 | 1.11 | 3.640 |
|  |  | 4.392 | 1.2$^a$ | 3.777 |

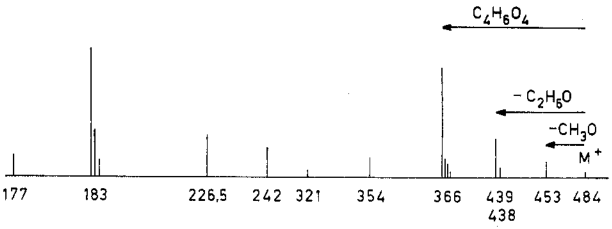


**Figure 7.** Mass spectrum of **13**.

**Hydrolysis of the Anhydrides. A. Results.** The anhydrides described in the preceding section were further identified by conversion into the corresponding dimethyl esters (Figure 5). A case in point was **12**, which, when treated with dilute base for 30 min, gave a pale yellow salt which furnished the diacid **14** upon acidification. This acid was rather unstable. As soon as it was formed it started to revert into **12**. Consequently **14** was isolated as quickly as possible and transformed directly into the dimethyl ester **13** by treatment with diazomethane. Relative to **12** the dimethyl ester was easier to handle and it could be chromatographed and recrystallized as in normal working-up procedures. However, its solubility was still too low to allow a well-resolved NMR spectrum to be obtained. Its mass spectrum is shown in Figure 7. The main features of this spectrum are typical for compounds related to dimethyl phthalate. Above its melting point or by treatment with 48% HBr **13** is transformed again into **12**. When **16** was treated with a dilute NaOH solution the corresponding disodium salt was easily obtained. Upon careful acidification a dark yellow compound, presumably the dibasic acid **17**, was obtained but before it could be filtered and dried it had reverted completely into **16**. The diacids **20** and **27** were much more stable. They can be stored for hours and are thermally stable to at least 100°. Clearly the stability of these diacids is of the following order (Figure 8).

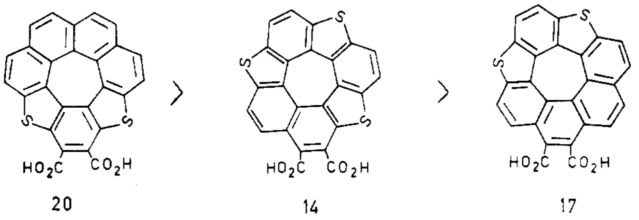


**Figure 8.**

**B. Discussion.** Phenanthrene-9,10-dicarboxylic acid (**33**) is unknown to date.[18] The instability of this compound is ascribed to the presence of β hydrogen atoms next to the carboxyl groups. These atoms are believed to bring the carboxyl groups closer together than, for instance, in phthalic acid. The angle between the C–COOH bond and the plane of the C=C bond is decreased to less than 123° (the corresponding angle in phthalic acid). The result is an increased interaction between the two carboxyl groups and consequently anhydride formation will be preferred. Bruice and Pandit[19] reported that the rate of anhydride formation is greatly enhanced when the free rotation of the reacting carboxyl groups is restricted. Molecular models show clearly that the β hydrogen atoms in **33** (Figure 9) indeed cause a

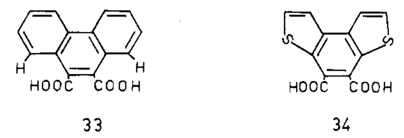


**Figure 9.**

**Table II**
**Mass Spectra of the Heterocirculenes**

| Compd | $M^+$ | M - S | M - $H_2S$ | M - CHS | M - $CH_3S$ | M - $C_2S_2$ | $M^{2+}$ |
|---|---|---|---|---|---|---|---|
| 7 | 100 | 2 | 2 | 2 | 4 | | 40 |
| 9 | 100 | | | 8 | | 3 | 80 |
| 8 | 100 | 2 | 4 | 3 | 3 | | 35 |
| 10 | 100 | 2 | 2 | 2 | 2 | | 50 |
| 11 | 100 | 2 | | 2 | 2 | | 32 |

restricted rotation of the carboxyl groups. However, these $\beta$ hydrogen atoms are no longer present in **34**, where the two outer benzene rings are replaced by thiophene rings. In this compound rotation is no longer restricted and as a result this acid is expected to be much more stable than **33**. This is in full accordance with the experimental results presented in this section.

**Decarbonylation of the Anhydrides. The Heterocirculenes.** The heterocirculenes were obtained by decarbonylation of the corresponding anhydrides (Figure 5). The decarbonylation could be effected either by prolonged boiling with copper powder in quinoline or by pyrolysis with soda lime. The first method gave poor results. The anhydrides were only partially decarbonylated and the heterocirculenes were not obtained in a yield higher than 20%. Decarbonylation with soda lime is a method used frequently in the synthesis of polyaromatics.[3b] Normally the anhydride is heated together with the soda lime at 400° for several hours and from the reaction mixture the hydrocarbon is removed by sublimation. The heterocirculenes described in this paper were stable enough to survive 400° and they were isolated by this method in about 50% yield.

The heterocirculenes crystallized from *p*-xylene in long, thin needles. They have a green-yellow color and show a weak fluorescence in solution. They do not melt but decompose very slowly above 350°. They are sparingly soluble in common organic solvents, making CAT NMR spectroscopy mandatory. From the circulene **8** a picrate (anthracite colored) was obtained which did not melt but instead decomposed over a wide range. The heterocirculenes show in their mass spectra as the only significant peaks the singly and doubly charged molecular ions. Low-intensity fragments $M - S^+$, $M - H_2S^+$, and $M - CHS^+$ could be detected. The mass spectral data of the heterocirculenes are collected in Table II.

**Structure Proof of the Heterocirculenes.** The conversion helicene → circulene represents in effect the addition of two carbon atoms to the helicene to form a new cyclic system containing an extra benzene ring. This means that identical circulenes can be prepared from different helicenes as indicated below (Figure 10). Based on this approach the circulene **9** was prepared from both the helicenes **35** and **36**. This two-way synthesis of **9** verifies unambiguously the structures of the heterocirculenes as well as the structures of the intermediate dehydrohelicenes.

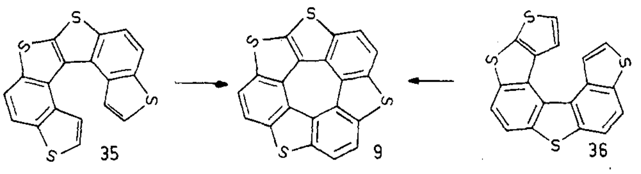


**Figure 10.**

**Synthesis of Thiacoronene.** Boekelheide[20] has recently reported the isolation of the heterocirculene **11**, called thiacoronene. It should be noted that **11** belongs theoretically to the corannulene class of circulenes, that is, it might be bowl shaped. It appeared that our route to thiacoronene, namely via the dehydrohelicene **37**, would allow **11** to be readily prepared. Nevertheless this apparently straightforward synthesis deserves some comment.

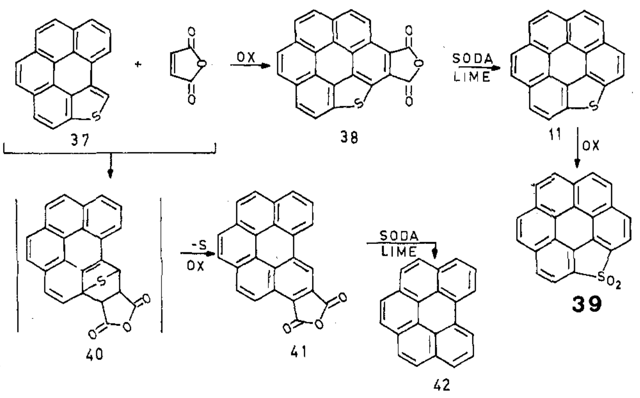


**Figure 11.**

The Diels–Alder addition of maleic anhydride to the dehydrohelicene **37** furnished a mixture of anhydrides (Figure 11). The presence of anhydride functions was demonstrated by ir spectroscopy. The mixture showed absorptions at 1820 and 1760 cm$^{-1}$. Elemental analysis of the purified anhydrides gave a lower sulfur percentage than calculated for **38**. The anhydride mixture was not purified any further, but was directly decarboxylated with soda lime. A careful analysis of the reaction mixture showed the presence of at least five products. Mass spectral analysis of the mixture showed molecular ions at *m/e* 350, 306, and 276. The compound with $M^+$ *m/e* 350 could not be isolated or identified. The compounds with $M^+$ *m/e* 306 and 276 could be obtained pure and were identified as **11** and **42**. The uv spectrum of thiacoronene was found to be identical with that recorded by Boekelheide[20] et al. The reason for the formation of more than two different anhydrides during the Diels–Alder addition is not understood at the moment. The presence of **42** as a reaction product can be explained by assuming a 1,4 addition of maleic anhydride to the thiophene ring of **37**.[21] From the intermediate **40** sulfur is lost and the resulting anhydride **41** is decarboxylated to **42**.

The values of the para-localization energies for the different sites of adduct formation in **37** are shown in Table I. These values support the possibility of a Diels–Alder addition to the thiophene ring of **37**. However, the very low yield in which **11** is formed cannot be blamed on this side reaction, because the calculations predict additions to take place almost exclusively at the 1,11 position. Thiacoronene sulfone (**39**) was obtained by oxidation of **11** with *m*-chloroperbenzoic acid in methylene chloride. Only 0.8 mg of **39** was obtained and from this material only a mass spectrum was taken. The spectrum is shown in Figure 12. This spectrum has an interesting feature. The sulfone loses little or no oxygen directly [1% relative abundance for (M − 16) peak, 3% for the (M − 32) peak]. Instead the most predominant peak in the spectrum, *m/e* 290, appears to be due to the formation of an oxacoronene ion **46** (Figure 13). A similar fragmentation has been observed in sulfones of a related structure.[22] However, the intensity of the fragmentation

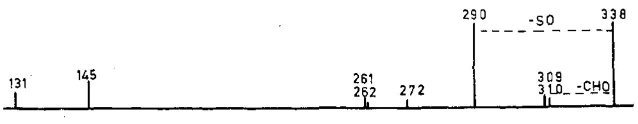


**Figure 12.** Mass spectrum of **46**.

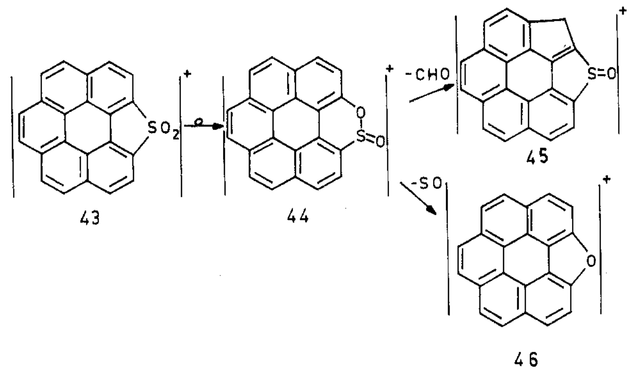
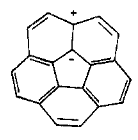


**Figure 13.**

representing **46** is unusually large, demonstrating the greater stability of the latter. The formation of the oxacoronene ion can best be explained[23] by a rearrangement of **43** to the cyclic sulfinate ester **44**, which either eliminates HCO or SO.

**Spectral Properties of the Heterocirculenes. NMR Spectra.** Charged structures like **3** and **47** may contribute



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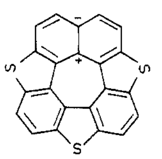

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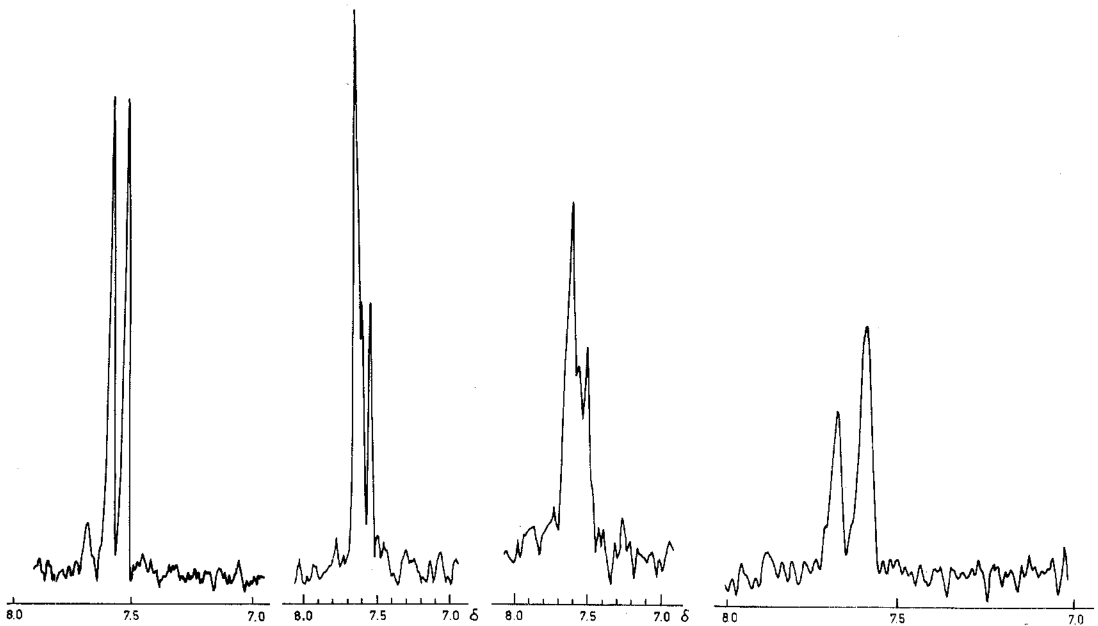
respectively to the ground state of **2** and **7**. If they do so, a direct influence of this charge distribution on the $^1$H and $^{13}$C chemical shifts in the NMR spectra is predicted.[24] However, Barth and Lawton[6] did not publish the $^{13}$C NMR spectrum of **2** and because of the limited solubility of the heterocirculenes in NMR solvents, no $^{13}$C NMR spectra of these molecules could be obtained. The $^1$H signal of **2** is found at δ 7.80 ppm, a value little changed from that of benzene. The $^1$H NMR spectra of the heterocirculenes are given in Figure 14. They all consist of multiplets centered about δ 7.6 ppm. These are normal values for condensed sulfur heterocycles. Hence, the $^1$H chemical shifts in the NMR spectra of the heterocirculenes give no significant indication for a polarization in the ground state.

**Uv Spectra.** The uv spectra of the heterocirculenes are drawn in Figure 15. The uv spectra of the [7]-heterocirculenes show resolved bands with much vibrational structure. They resemble the uv spectra of the corresponding dehydrohelicenes.[12] Relative to those dehydrohelicenes a 10–20-mμ red shift of the longest wavelength band is observed. A much larger red shift is observed when the longest wavelength band of a thiophthene[25] containing heterocirculene is compared with those of its corresponding dehydrohelicene.[12] Red shifts up to 62 mμ were found. The uv spectrum of **9** does not differ essentially from that of **7**![12] To account for these results the uv spectra of **7** and **9** were calculated[26] by PPP type of semiempirical SCF–MO calculations.[27] In these calculations, limited configuration interaction was employed by taking into account all singly excited states corresponding to excitation of an electron from the four highest occupied orbitals into the four lowest vacant orbitals. In the calculations the molecules were assumed to be flat and the geometry was based on the known bond lengths and bond angles of thiophene[28] and benzene.[29] Electron repulsion integrals were evaluated with the aid of the Nishimoto and Mataga[30] approximation. The variable $\beta$ modification of the PPP method[31] has been employed, using the following parameters:[32] $I_c = 11.22$, $\gamma_{cc} = 10.53$ and $\beta_{cc} = -0.51p - 1.84$ eV; $I_s = 20.00$, $\gamma_{ss} = 10.84$ and $\beta_{cs} = -1.625$ eV. The results are given in Tables III and IV.

As can be seen from the results in Table IV, the calculations predict the general features of the uv spectra very well. The uv spectrum of thiacoronene (**11**) corresponds very closely to that of coronene[2] itself. It is almost identical with respect to the nature and position of the absorption bands. The intensity of the absorption bands differs somewhat. Relative to coronene the $\alpha$ band has a higher and the $\beta$ band a lower intensity.

**ESR Spectra.** Radical anions of the heterocirculenes **7** and **9** were obtained by electrolysis in DMF. They were generated in a $10^{-3}$ *M* solution at a constant current of 10 μA. Using this procedure $10^{-2}$ *M* supporting electrolyte



60 Mc NMR spectrum of 7 in CS$_2$(350 scans)

60 Mc NMR spectrum of 8 in CS$_2$ (424 scans)

60 Mc NMR spectrum of 10 in CS$_2$ (194 scans)

60 Mc NMR spectrum of 9 in CS$_2$(700 scans)

**Figure 14.**

### Table III
### Experimental and Calculated Transitions of the Heterocirculenes 7 and 9 ($\lambda_{max}$, mμ)

| Compd | Experimental<br>nm (log ε) | Calculated<br>nm (*f*) |
|---|---|---|
| **9** | 425 (2.92), 399 (3.14), 383 (3.60), 363 (3.55), 233 (4.32), 318 (4.20), 288 (4.47), 275 (4.65) | 390 (0.05), 348 (0.06), 336 (0.29), 323 (0.72), 292 (0.01), 283 (0.48), 280 (1.61), 274 (0.29), 264 (0.53), 257 (0.00), 256 (0.05), 252 (0.04), 230 (0.07), 226 (0.15) |
| **7** | 431 (2.40), 408 (2.90), 387 (3.25), 369 (3.35), 357 (3.54), 311 (3.82), 289 (4.10), 258 (4.40), 240 (4.20) | 390 (0.04), 366 (0.16), 359 (0.38), 352 (0.14), 299 (0.83), 287 (0.54), 286 (0.24), 282 (0.18), 276 (0.04), 275 (0.47), 257 (0.98), 254 (0.70), 238 (0.17), 233 (0.11) |

### Table IV
### The Red Shift Δλ of the Longest Wavelength Absorption of the Heterocirculenes Relative to the Corresponding Dehydrohelicenes

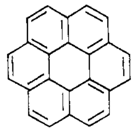
| Compds | Δλ obsd, mμ | Δλ calcd, mμ |
|---|---|---|
| 6 → 7 | 18 | 6 |
| 25 → 9 | 49 | 30 |
| 22 → 9 | 62 | 40 |

### Table V
### Splitting Constants of the Circulene Radical Anions

| Compd | Splitting constants, G | | | | |
|---|---|---|---|---|---|
| | $a_{H1}$ | $a_{H2}$ | $a_{H3}$ | $a_{H4}$ | |
| 7 | 2.0 | 0.2 | 1.25 | 3.35 | obsd |
| | 1.494 | −0.348 | 1.316 | 5.959 | calcd |
| 9 | 2.6 | 0.5 | 3.8 | | obsd |
| | 3.071 | 0.420 | 3.289 | | calcd |

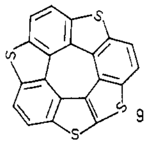
tetraethylammonium perchlorate (TEAP) was suitable. The resulting ESR spectra of the radical anions of **7** and **9** are shown in Figure 16. The assignment of the different hyperfine splitting constants was made by comparing them with the theoretical values obtained by McLachlan's approximate SCF method[33] and the McConnell relationship.[34] The results are summarized in Table V.

**Correlation between Nonplanarity and Optical Activity. Preparation of a Methylated Circulene.** Optical activity of a suitable circulene would be prima facie evidence for nonplanarity. Nonplanar circulenes can be bowl shaped or corrugated and a qualitative way to discriminate between these molecules is based on the geometry of the aromatic rings from which the circulene is constructed. The internal angle (the angle between two carbon–carbon double bonds) of a benzene ring is 60°, whereas those for thiophene[35a] and furan[35b] are 45 and 30°, respectively (Figure 17). In order to obtain a circulene which is approximately strain-free the sum of these angles need to be 360°. This is the case in coronene (**1**) and in the heterocirculene **9**. We



1

360° = 6 × 60°



9

360° = 3 × 60° + 4 × 45°

know from coronene that it is a planar molecule[5] and most probably **9** is also planar. When the sum of the individual internal angles differs from 360° the construction of a circulene will be attended with introduction of additional strain energy. The difference between bowl-shaped and corrugated circulenes is that in the former the sum of these angles is less than 360° and in the latter more than 360°. In corannulene (**2**) this sum is 300° (5 × 60°), whereas in the [7]-circulene **4** it is 420° (7 × 60°). For obvious reasons in our attempts to demonstrate nonplanarity of the heterocirculenes we concentrated our attention on the heterocirculene **8**, in which the sum of the internal angles (390°) deviates most from 360°. However, **8** had to be substituted in order to make it dissymetric. A substitution reaction of this type had to conform to the following requirements: (a) result in a compound which had an unequivocal substitution pattern, (b) furnish the substituted compound in high yield. A compound with an unequivocal substitution pat-

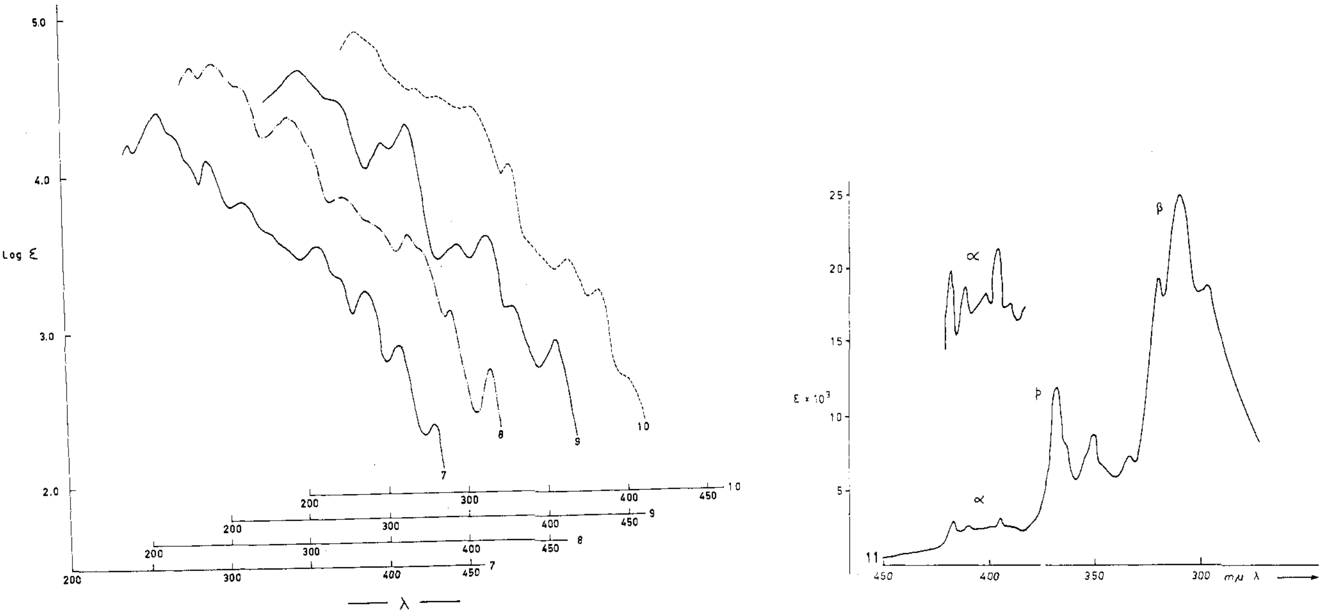


**Figure 15.** The uv spectra of the heterocirculenes in $CHCl_3$.

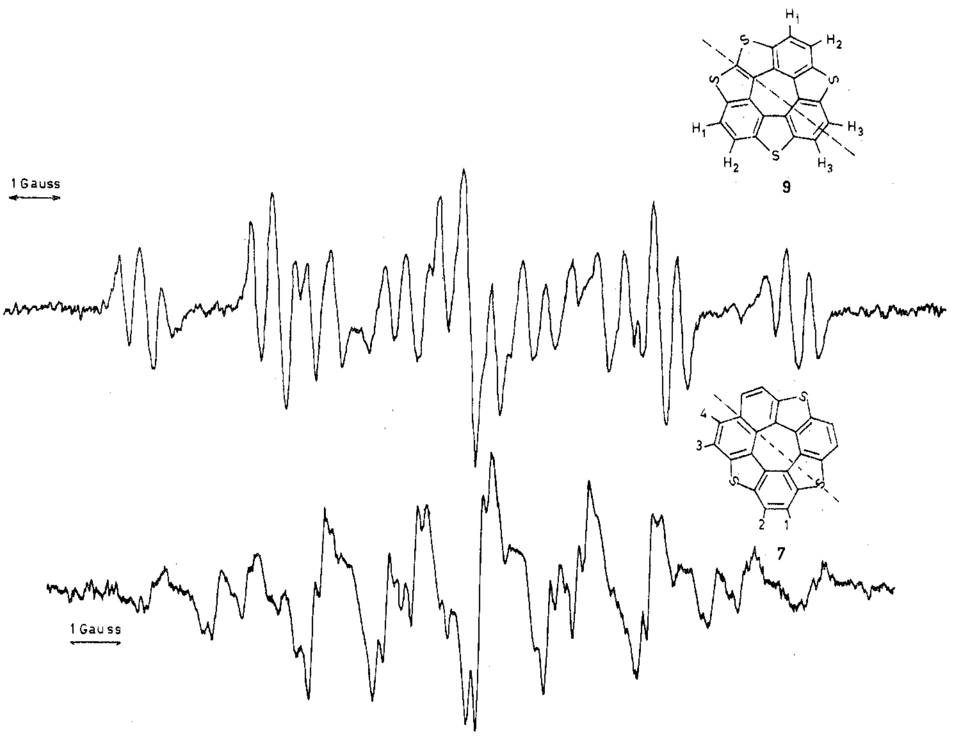


**Figure 16.** ESR spectra of the radical anions of 7 and 9.

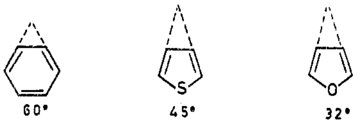


**Figure 17.**

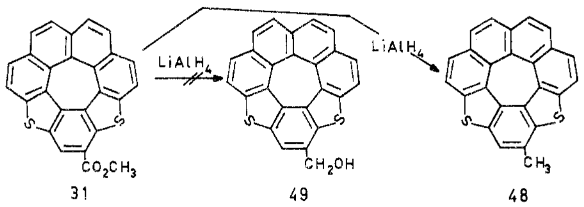
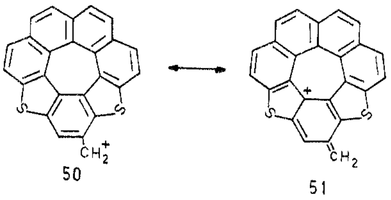


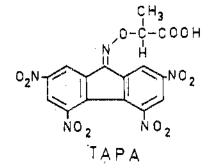
**Figure 18.**

tern had been realized in the synthesis of **31**. The methylated circulene **48** was a suitable compound for the resolution experiments. Therefore we directed our attention to the conversion of **31** into **48**. This could be achieved in a very simple one-step reduction. Treatment of **31** with $LiAlH_4$ under normal reaction conditions did not furnish **49** (as expected), but yielded almost quantitatively **48** (Figure 18). This reaction is thus a rare example of a one-step reduction of an ester to the corresponding hydrocarbon initiated by a metal hydride only.[36] Closely related reactions are found in reports of reductions with $LiAlH_4$–$AlCl_3$.[37] The reduction procedure is believed to involve carbonium ion intermediates. Thus, the reaction described above provides an indication of the relatively great stability of the intermediate carbonium ion **50**. The aromatization to the inner seven-membered ring in structure **51** might explain this.



50 51

**Diastereomeric Complex Formation.** In the attempted resolution of **48** we followed the procedure which had been developed by Newman for the resolution of hexahelicene.[38] When a solution of the circulene **48** in benzene was treated with 1 equiv of (+)-TAPA, $[\alpha]^{20}{}_{436}$ +432°, the solution became green. The uv spectrum of the resulting solution was recorded and the spectrum shown in Figure 19 was obtained. A broad absorption band with a maximum at 570 mμ was observed. Neither **48** nor TAPA separately exhibit an absorption above 450 mμ, a clear indication for the pres-



TAPA

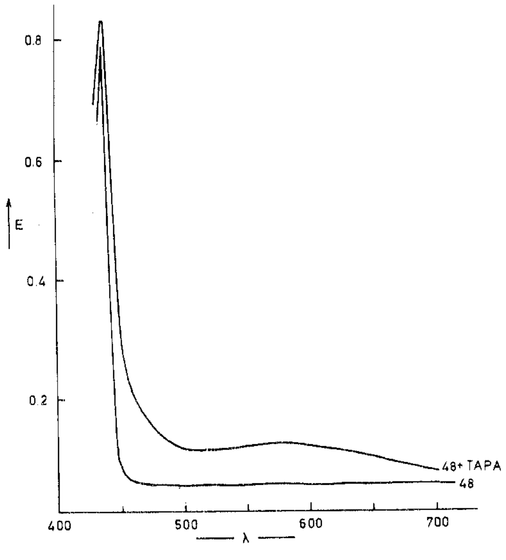


**Figure 19.** Uv spectra of 48 and of 48 + TAPA (1:1 molar) in $C_6H_6$.

ence of a charge-transfer complex. In the actual resolution experiment **48** was treated with 0.5 equiv of (+)-TAPA. Upon the addition of ethanol some of the circulene separated as yellow needles. A further application of this treatment afforded a small quantity of **48**, which showed no optical rotation (measured at 436, 546, and 578 mμ). We repeated the experiments at lower temperature. Both the circulene and TAPA were soluble in 1,2-dichloroethane at −30°. Solutions of **48** and (+)-TAPA were mixed at 25° and some ethanol was added. The solution was cooled carefully to −30°, after which the circulene started to crystallize. The circulene crystals were isolated and then redissolved in $CS_2$ at −30°. Again no optical rotation was observed. A small quantity (0.9 mg) of the circulene TAPA complex could be obtained in crystalline form when the experiments were carried out in chloroform. The measured rotation of this complex was $\alpha^{20}{}_{436}$ +0.025°. From this complex the circulene could be regained by addition of ethanol, but again no optical rotation was observed. The experiments described above were repeated with the circulene **10**. The same negative results were obtained.

## Discussion

A few comments about these negative results are in order.

Three particular factors may be invoked to explain the failure of the resolution experiments:

(1) adjustments of bond lengths and bond angles keep a circulene planar;

(2) the circulenes are nonplanar, but inversions occur at such a rate that resolution is prevented;

(3) the method used for the resolution was not the appropriate one.

Inversions of a corrugated circulene can proceed via a planar transition state or via an undulating motion which passes through the whole molecule. It is very difficult to differentiate between these two modes of inversion and until experimental proof concerning possible nonplanarity of our heterocirculenes is available further predictions about this subject seem useless.[40] Concerning the resolution method: [7]-heterocirculenes readily form charge-transfer complexes in which the former function as donor molecules (see Experimental Section). This may be ascribed to a partial aromatization of the inner seven-membered ring which of course promotes planarity of the molecule. Moreover, it is known that in some cases formation of charge-transfer complexes enhances greatly the rate of racemization.[41] This diminishes to some extent the importance of our resolution experiments with TAPA.

## Experimental Section

All reagents were purified where necessary by standard methods. For column chromatography neutral alumina (Merck $A_1$) or silica gel (B. D. H.) was used. Melting points (corrected) up to 300° were determined on a Mettler $FP_1$ microscope and between 300 and 350° (uncorrected) on a Reichert hot-stage apparatus. Uv spectra were measured on a Zeiss PMQ 11 or recorded with a Beckman DB-G grating spectrophotometer. NMR spectra were obtained with a Varian A-60D instrument, using tetramethylsilane as an internal standard. The chemical shifts are expressed in δ values (parts per million). Mass spectra were obtained with a AEI MS 902 instrument and recorded by Mr. A. Kiewiet. The ESR spectra were recorded on a Varian $E_4$ spectrometer. Elemental analyses were carried out by Mr. H. Draayer, Mr. J. Ebels, and Mr. J. Vos in the microanalytical department of this laboratory. Optical activity was measured on a Zeiss Lichtelektrisches Präzisionspolarimeter 005 using 5- or 10-cm cells.

**9,10-Epithio-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*cdef*]fluorene-1,2-dicarboxylic Anhydride (12).** The dehydrohelicene **6** (50 mg, 0.15 mmol), chloranil (125 mg, 0.51 mmol), and maleic anhydride (750 mg, 7.7 mmol) were mixed together in a 50-ml reaction flask. The flask was equipped with an air condenser and the flask contents were brought under a nitrogen atmosphere. The flask was put into a molten metal bath of 220° and the reaction mixture was refluxed for 2 hr. After cooling, 20 ml of *p*-xylene was added and the resulting suspension was refluxed for an additional 10 min. After cooling, the orange-red anhydride was filtered, washed thoroughly with *p*-xylene and ether, and dried in vacuo. The analytically pure anhydride **12** (mp >400°) was obtained by sublimation (350–400°, $10^{-4}$ mm). The yield of **12** was 43 mg (65%).

Anal. Calcd for $C_{24}H_6S_3O_3$: C, 65.74; H, 1.38; S, 21.93. Found: C, 65.8; H, 1.6; S, 21.9.

Ir (KBr) 1825, 1772, 1220, 1149, 895, and 790 $cm^{-1}$.

**9,10-Epithio-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*cdef*]fluorene-1,2-dicarboxylic Acid Dimethyl Ester (13).** To 15 ml of a 10% sodium hydroxide solution was added 15 mg ($3.4 \times 10^{-2}$ mmol) of the anhydride **12**. The mixture was boiled for 30 min. After cooling, the pale yellow salt was hydrolyzed by acidification with dilute hydrochloric acid. The pale yellow diacid **14** was filtered, washed with water until neutral, and dried quickly in vacuo. After drying, the acid was transferred into a 50-ml reaction flask and a solution of an excess of diazomethane in ether was added. After 30 min of stirring excess of diazomethane was destroyed with some acetic acid, after which the solvent was removed at reduced pressure. The ester was taken up in a minimum of hot chloroform and chromatographed on alumina with chloroform. After removal of the solvent, the residue was recrystallized from carbon tetrachloride, yielding 12 mg (73%) of the pure diester **13** (mp 308–309°).

Anal. Calcd for $C_{26}H_{12}S_3O_4$: C, 64.45; H, 2.49. Found: C, 64.3; H, 2.6.

Ir (KBr) carbonyl absorptions at 1711, 1720 $cm^{-1}$; NMR ($CD_2Cl_2$, CAT) 3 H δ 4.06 (s), 3 H 4.08 (s), 4 H 7.41 (m), 2 H 7.54 ppm (m); uv ($CHCl_3$) $\lambda_{max}$ (log ϵ) 450 (2.88), 384 (3.68), 332 (3.83), 318 (s) (3.90), 304 (4.23), 294 (4.29) 288 (4.28), 262 (4.51).

The other anhydrides and diesters were obtained by an analogous procedure to that described for the preparation of **12** and **13.**

**9,10-Etheno-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*cdef*]fluorene-9,10-dicarboxylic Anhydride (16).** The anhydride **16** (mp >400°) was obtained from the dehydrohelicene **15** (50 mg, 0.15 mmol). The yield of **16** was 11 mg (17%).

Anal. Calcd for $C_{26}H_8O_3S_2$: C, 72.21; H, 1.87. Found: C, 72.2; H, 2.0.

Ir (KBr) 1824, 1763, 1220, 1156, 918, 828, and 801 $cm^{-1}$.

When the anhydride **16** was boiled with dilute sodium hydroxide solution a yellow disodium salt was readily formed. However, after careful acidification **16** was reformed immediately.

**9,10-Etheno-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*cdef*]fluorene-4,5-dicarboxylic Anhydride (19).** The anhydride **19** (mp >400°) was obtained from the dehydrohelicene 18 (40 mg, 0.12 mmol). The yield of **19** was 31.2 mg (60%).

Anal. Calcd for $C_{26}H_8O_3S_2$: C, 72.21; H, 1.87; S, 14.83. Found: C, 72.2; H, 2.0; S, 14.4.

Ir (KBr) 1824, 1769, 1221, 1186, 888, 852, 741, and 550 $cm^{-1}$.

**9,10-Etheno-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*cdef*]fluorene-4,5-dicarboxylic Acid Dimethyl Ester (21).** The dimethyl ester **21** (mp 320–322°) was obtained from the anhydride **19** (5 mg, $1.2 \times 10^{-2}$ mmol). The yield of **21** was 4.4 mg (76%): calcd mol wt 478.033 (found by mass spectrometry, M 478.035); ir (Nujol) carbonyl absorptions at 1722, 1710 $cm^{-1}$.

**1,11-Etheno-6,7-epithio-2,5,8-trithiabenz[3.4]azuleno[5,6,-7,8-*jkl*]-*as*-indacene-1,2-dicarboxylic Anhydride (26).** The anhydride **26** (mp >400°) was obtained from the dehydrohelicene **25** (30 mg, $8.5 \times 10^{-2}$ mmol). The yield of **26** was 23 mg (61%).

Anal. Calcd for $C_{22}H_4S_4O_3$: C, 59.44; H, 0.91; S, 28.85. Found: C, 60.0; H, 1.2; S, 28.3.

Ir (KBr) 1830, 1772, 1233, 1186, 905, and 802 $cm^{-1}$.

**1,11-Etheno-6,7-epithio-2,5,8-trithiabenz[3.4]azuleno[5,6,-7,8-*jkl*]-*as*-indacene-1,2-dicarboxylic Acid Dimethyl Ester (28).** The dimethyl ester **28** (mp 338–342° dec) was obtained from the anhydride **26** (7.4 mg, $1.7 \times 10^{-2}$ mmol). The yield of **28** was 5.7 mg (68%): calcd mol wt for $C_{24}H_{10}O_4S_4$, M 489.946 (found by mass spectrometry, M 490); ir (Nujol) carbonyl absorptions at 1733, 1714 $cm^{-1}$.

**1,11-Etheno-6,7-epithio-2,5,8-trithiabenz[3.4]azuleno[5,6,-7,8-*jkl*]-*as*-indacene-8,9-dicarboxylic Anhydride (23).** The anhydride **23** (mp >400°) was obtained from the dehydrohelicene **22** (70 mg, $2.10^{-1}$ mmol). The yield of **23** was 65 mg (73%).

Anal. Calcd for $C_{22}H_4S_4O_3$: C, 59.44; H, 0.91; S, 28.85. Found: C, 59.5; H, 0.9; S, 28.9.

Ir (KBr) 1829, 1773, 1276, 1207, 1182, 1172, 920, 891, 794, and 746 cm$^{-1}$.

**1,11-Etheno-6,7-epithio-2,5,8-trithiabenz[3.4]azuleno[5,6,-7,8-*jkl*]-*as*-indacene-8,9-dicarboxylic Acid Dimethyl Ester (24).** The dimethyl ester **24** (mp 320–324°) was obtained from the anhydride **23** (4.5 mg, 1.10$^{-1}$ mmol). The yield of **24** was 4.0 mg (82%): calcd mol wt for $C_{24}H_{10}O_4S_4$, M 489.946 (found by mass spectrometry, M 489.947); ir (Nujol) carbonyl absorptions at 1718 and 1703 cm$^{-1}$.

**1,11-Etheno-2,5,6-trithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,-7,6-*ijkl*]-*as*-indacene-1,2-dicarboxylic Anhydride (30).** The anhydride **30** (mp >400°) was obtained from the dehydrohelicene **29** (70 mg, 0.2 mmol). The yield of **30** was 42 mg (48%).

Anal. Calcd for $C_{24}H_6S_3O_3$: C, 65.74; H, 1.38; S, 21.93. Found: C, 66.3; H, 1.7; S, 21.1.

Ir (KBr) 1825, 1769, 1231, 1171, 904, and 812 cm$^{-1}$.

**9,10-Epithio-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,-7,6-*cdef*]fluorene (7). A. By Soda Lime Decarboxylation.** The anhydride **12** (50 mg, 0.11 mmol) and soda lime (700 mg) were ground together and transferred into a sublimation apparatus. The reaction mixture was brought carefully under a nitrogen atmosphere and heated to 350° for 45 min. After cooling the sublimation apparatus was evacuated (2 × 10$^{-3}$ mm) and heated again to 380–420° for 4 hr. The circulene (22 mg, 6.0 × 10$^{-2}$ mmol) sublimed in yellow-green needles. Analytically pure **9** (mp 400–410° dec) was obtained by recrystallization from *p*-xylene.

Anal. Calcd for $C_{22}H_8S_3$: C, 71.71; H, 2.19. Found: C, 71.8; H, 2.2.

**B. By Cu–Quinoline Decarboxylation.** The anhydride **12** (40 mg, 9 × 10$^{-2}$ mmol) was added to a suspension of 50 mg of Cu powder in 10 ml of quinoline. The mixture was heated at 240° for 24 hr. After cooling the reaction mixture was diluted with chloroform (50 ml). The organic solution was extracted with 2 *N* hydrochloric acid (6 × 20 ml), water, and sodium bicarbonate solution. After drying, filtering, and evaporation of the solvent, the residue was chromatographed on alumina with benzene. The eluate gave upon concentration 12 mg (36%) of the circulene **9**.

The circulenes **8**, **9**, and **10** were obtained by a similar procedure as that described for the preparation of **7**.

**1,11-Etheno-6,7-epithio-2,5,8-trithiabenz[3.4]azuleno[5,6,-7,8-*jkl*]-*as*-indacene (9). A. By Soda Lime Decarboxylation of the Anhydride 23 (50 mg, 0.11 mmol).** The yield of the circulene **9** (mp 460° dec) was 21.1 mg (51%).

**B. By Cu–Quinoline Decarboxylation of the Anhydride 23 (70 mg, 0.16 mmol).** The yield of the circulene **9** was 8 mg (13.3%).

**C. By Soda Lime Decarboxylation of the Anhydride 26 (33 mg, 7.4 × 10$^{-2}$ mmol).** The yield of the circulene **7** was 12 mg (42.9%).

**D. By Cu–Quinoline Decarboxylation of the Anhydride 26 (150 mg, 0.34 mmol).** The yield of the circulene **7** was 16.5 (13%).

Anal. Calcd for $C_{20}H_6S_4$: C, 64.14; H, 1.61. Found: C, 64.1; H, 1.6.

**9,10-Etheno-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*cdef*]fluorene (8). A. By Soda Lime Decarboxylation of the Anhydride 16 (9.2 mg, 2.1 × 10$^{-2}$ mmol).** The yield of the circulene **8** was 2.3 mg (23%).

**B. By Soda Lime Decarboxylation of the Anhydride 19 (80 mg, 0.18 mmol).** The yield of the circulene **8** (mp 410° dec) was 35 mg (54%).

Anal. Calcd for $C_{24}H_{10}S_2$: C, 79.51; H, 2.78; S, 17.69. Found: C, 79.4; H, 2.8; S, 17.7.

**Picrate of Circulene 8.** To a stirred solution of **8** (10 mg) in *p*-xylene (10 ml) was added dropwise a solution of picric acid (10 mg) in absolute ethanol (3 ml); the solution was refluxed for 10 min, cooled, and allowed to stand overnight. The almost black colored needles were filtered, washed with ethanol, and dried in vacuo. The crystals decomposed above 238°.

Anal. Calcd for $C_{30}H_{13}N_3O_7S_2$: N, 7.10. Found: N, 6.6.

**1,11-Etheno-2,5,6-trithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*ijkl*]-*as*-indacene (10). By Soda Lime Decarboxylation of the Anhydride 30 (49 mg, 0.11 mmol).** The yield of the circulene **10** (mp 390° dec) was 20 mg (50%).

Anal. Calcd for $C_{22}H_8S_3$: C, 71.71; H, 2.19; S, 26.10. Found: C, 71.8; H, 2.3; S, 25.9.

**Thiacoronene (11).** The Diels–Alder reaction was carried out with the dehydrohelicene **37** (70 mg, 0.25 mmol), chloranil (160 mg), and maleic anhydride (950 mg). At the end of the reaction a dark-brown mixture of anhydrides was obtained, which were not identified at that stage. The crude mixture was used for the soda lime decarboxylation.

The anhydrides (72 mg) and soda lime (1 g) were ground together and transferred to a sublimation apparatus. The mixture was brought under a nitrogen atmosphere and heated at 370° for 1 hr. After evacuation of the apparatus (10$^{-2}$ mm) the mixture of polyaromatics started to sublime over a long range of bath temperatures (300–460°). The reaction products were dissolved in benzene and chromatographed on alumina with benzene. This yielded 18 mg of yellow-green material and TLC analysis of this mixture showed the presence of at least four different products. These products could be separated using preparative thick layer chromatography on alumina with benzene–cyclohexane (1:5) as eluting agent. The compound with the highest $R_f$ value could be identified as thiacoronene. Pure **11** (3 mg) was obtained by recrystallization from methylcyclohexane. Thiacoronene starts to sublime at 262°. The crystals soften at 326° and melt above 350°: calcd mol wt for $C_{22}H_{10}S$, M 306.050 (obtained by mass spectrometry, M 306.051).

**Thiacoronene 3,3-Dioxide (39).** To a stirred solution of thiacoronene (1 mg) in $CH_2Cl_2$ (2 ml) was added excess *m*-chloroperbenzoic acid (6 mg). Stirring was continued for 5 hr, after which the solution was filtered and 10 ml of cold methanol was added. The precipitated sulfone **39** (0.7 mg) was collected and dried. From this material only a mass spectrum was taken.

**9,10-Etheno-3,6-dithianaphth[2′.1′.8′:3.4.5]azuleno[1,8,7,6-*cdef*]fluorene-4-carboxylic Acid Methyl Ester (31).** To a solution of **18** (58 mg, 0.21 mmol) in hot *p*-xylene (10 ml) was added methyl propiolate (5 ml) and chloranil (60 mg). After the addition the solution was refluxed for 3 days and after cooling the precipitate was filtered, washed with benzene and ether, and dried in vacuo. The solid was taken up in a minimum of hot *p*-xylene and chromatographed on alumina with chloroform. After removal of the solvent the residue was recrystallized from *p*-xylene. This yielded 43 mg (60%) of the pure ester **31** (mp 309–311°): calcd mol wt for $C_{26}H_{12}O_2S_2$, M 420.0279 (found by mass spectrometry, M 420.0289); ir (Nujol) most important absorptions at 1696, 1292, 1249, 1202, and 845 cm$^{-1}$.

Decarboxylation of the acid **32** with soda lime according to the general procedure yielded the circulene **18** in 45% yield.

**ESR Spectra. Electrolytic Reduction.** The spectra were recorded in a flat cell with a platinium gauze cathode at the bottom of the flat area and a platinum anode in the middle of the cell. The cell was provided with a variable direct current supply. After degassing with dry nitrogen, radical anions could be detected at 10-$\mu$A solutions in DMF with TEAP as the supporting electrolyte.

**Reduction of 31 with $LiAlH_4$.** To a suspension of 500 mg of $LiAlH_4$ in dry THF (15 ml) was added dropwise with vigorous magnetic stirring 21.8 mg (5.2 × 10$^{-2}$ mmol) of the methyl ester **31** in 125 ml of dry THF. After the addition was complete the reaction mixture was refluxed for 18 hr. The reaction flask was cooled in an ice bath and the $LiAlH_4$ was destroyed by the careful addition of some water. Subsequently 10 ml of a 4*N* HCl solution and 50 ml of benzene were added. After extraction the benzene layer was separated and washed with water and $NaHCO_3$ solution. After drying ($MgSO_4$), filtering, and evaporation of the solvent the residue was taken up in a minimum of hot *p*-xylene and chromatographed on alumina with benzene. After removal of the solvent the residue was recrystallized from benzene. The yield of **48** (mp 335° dec) (17.2 mg) was 88%.

Anal. Calcd for $C_{25}H_{12}S$: C, 79.74; H, 3.21. Found: C, 79.9; H, 3.4.

Uv ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 436 (2.72), 412 (3.06), 384 (3.51), 363 (3.51), 342 (3.64), 323 (4.10), 312 (4.30), 296 (4.18), 281 (4.52), 264 (4.68), 249 (4.65).

**Attempted Resolution of 48. A.** To a refluxing solution of **48** (7.951 mg, 2.1 × 10$^{-2}$ mmol) in 2 ml of benzene was added (+)-TAPA (4.271 mg, 9.5 × 10$^{-3}$ mmol) in 4 ml of benzene. The solution became directly green colored. Refluxing was continued for an additional 10 min and after cooling 3 drops of ethanol was added to the solution. After standing for 2 days at room temperature the precipitated circulene (4.312 mg) was filtered, washed with benzene and ethanol, and dried in vacuo. This material (dissolved in 4 ml of $CHCl_3$) showed no optical rotation. To the mother liquor was added an additional 3 ml of ethanol. The precipitated circulene (2.013 mg) was collected and washed as before. This material showed also no optical rotation.

**B.** To a suspension of **48** (11.0 mg, 2.9 × 10$^{-2}$ mmol) in dichloroethane (5 ml) was added a solution of (+)-TAPA (9.3 mg, 2.1 × 10$^{-2}$ mmol) in 6 ml of dichloroethane. The resulting green-colored solution was cooled at −30° for 24 hr. Ethanol (4 ml) was added and cooling was continued for an additional 3 days. The crystallized circulene (4.23 mg) was separated from the solution by decantation, thoroughly washed with ethanol, and then redissolved in carbon disulfide (6 ml) which was previously cooled to −50°. The solution was transported to a thermostated cell in which the temperature was kept at −30°. Again no optical rotation was observed.

**C.** To a solution of 48 (4.651 mg, 12.5 × $10^{-3}$ mmol) in chloroform (10 ml) was added (+)-TAPA (3.578 mg, 8 × $10^{-3}$ mmol) in chloroform (2 ml). The resulting solution was refluxed for 5 min and half of the chloroform (6 ml) was removed by distillation. After cooling and standing for 48 hr, the precipitated complex (0.988 mg) was separated from the solution by decantation and washed with 1 ml of cold chloroform. The solid was dried and then dissolved in 4 ml of chloroform and the rotation was measured. The observed values were $\alpha_{436}$ 0.025°, $\alpha_{546}$ 0.005°, and $\alpha_{578}$ <0.005°. After removal of the chloroform and addition of 5 ml of ethanol the resulting circulene (0.314 mg) was filtered and washed with benzene–ethanol. This material showed no optical rotation.

**Registry No.**—**6,** 30689-70-4; **7,** 35817-61-9; **8,** 54844-47-2; **8** picrate, 54844-48-3; **9,** 54844-49-4; **10,** 54844-50-7; **11,** 40516-55-0; **12,** 35817-59-5; **13,** 35817-60-8; **15,** 30689-69-1; **16,** 54844-51-8; **18,** 54844-52-9; **19,** 54844-53-0; **21,** 54869-88-4; **22,** 54844-54-1; **23,** 54844-55-2; **24,** 54844-56-3; **25,** 54844-57-4; **26,** 54844-58-5; **28,** 54844-59-6; **29,** 54844-60-9; **30,** 54844-61-0; **31,** 54844-62-1; **37,** 54844-63-2; **39,** 54844-64-3; **48,** 54869-87-3; maleic anhydride, 108-31-6; methyl propiolate, 922-67-8; $LiAlH_4$, 16853-85-3.

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# Polymeric Reagents. IV.[1] Synthesis and Utilization of an Insoluble Polymeric Organotin Dihydride Reagent

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*Received February 11, 1975*

The preparation of an insoluble polymeric hydride reagent has been achieved by the incorporation of *n*-butyltin dihydride functional groups onto a macroreticular polystyrene matrix. Reaction of the polymeric organotin dihydride reagent with iodooctane indicated the minimum hydride content to average 2.0 mmol/g of polymer. Utilization of the reagent for the reduction of aldehydes and ketones to alcohols and the reduction of halides to hydrocarbons is discussed. The selective reduction of only one functional group of a symmetrical difunctional aldehyde (terephthaldehyde) is also demonstrated. The regeneration and stability of the reagent are also discussed.

The chemical industry is being faced with the ever-increasing problems of pollution control and a scarcity of raw materials. Recent developments[1,3] in the area of insoluble, regeneratable reactive polymers has resulted in the availability of many new reagents with unique properties that are capable of providing solutions to these problems. Despite the growing list of polymers that have been used to effect oxidation, hydrogenation, alkylation, etc., there has been no report of a general reducing agent possessing a wide range of applications. We now describe our efforts di-