Synthesis and Resolution of Some Heterohelicenes[1]

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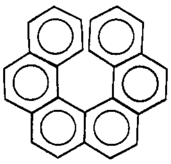
Photolysis of a number of 1,2-di(hetaryl)ethenes in which the hetaryl groups were benzo[*b*]thien-2-yl, naphtho[2,1-*b*]thien-2-yl, naphtho[2,1-*b*]furan-2-yl, or benzo[1,2-*b*:4,3-*b*′]dithien-2-yl in benzene solution in the presence of a trace of iodine produced heterocyclic analogs of penta-, hexa-, and heptahelicene. A heptaheterohelicene was obtained also by a double photocyclization reaction. Three of these compounds were resolved by crystal picking, whereas in one case resolution also was achieved by recrystallization from an optically active solvent. The observed specific optical rotations were extremely high. The structure of the helicenes followed clearly from the nmr spectra by the presence of strongly shielded protons. The mass spectra of the heterohelicenes gave evidence for the formation of planar ions upon electron impact. An undecaheterohelicene **32**, both racemic and partially resolved, was prepared.



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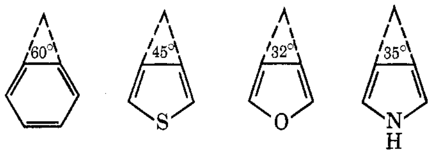
Ever since the synthesis of hexahelicene[2] (phenanthro[3,4-*c*]phenanthrene, **1**) by Newman and Lednicer,[3] this compound has attracted a great deal of attention. As can be seen easily the hexahelicene molecule cannot be planar because of the steric interference ("overcrowding") of the terminal benzene rings. The assumption that the actual shape resembles that of a helix was confirmed recently by X-ray analysis.[4] Hexahelicene, being the archtype of an inherently dissymmetric chromophore,[5] exhibits a very high specific optical rotation, $[\alpha]^{25}\mathrm{D}$ +3707° (CHCl$_3$). This fact coupled with the relative simplicity of the hexahelicene molecule prompted many investigators to apply various existing theories relating molecular structure and optical activity to this compound.[6] The results, however, were contradictory, some predicting the right-handed[7] helicene to produce a negative rotation[6a] while others predicted the opposite sign.[6b–d]

The laborious synthesis and the unique but difficult resolution of hexahelicene limited extensive study of this compound and simpler methods have been examined especially by Martin and coworkers. They successfully applied the cyclization reaction of Hewett to the synthesis of hexahelicene carboxylic acids.[8] Versatile routes to unsubstituted hexahelicene and its benzologs hepta-, octa-, and nonhelicene were reported also;[9] the key step in these syntheses is a photocyclization reaction analogous to the well-known photochemical ring closure of stilbene to phenanthrene.[10] The nmr spectra of the helicenes, which were very markedly affected by the overcrowding, were investigated in detail (computer simulation).[11]

Recently Martin and coworkers reported the synthesis of tridecahelicene[12] and of an azahexahelicene.[13] It must be emphasized that phenanthrene, benzo[*c*]-phenanthrene, and dibenzo[*c*,*g*]phenanthrene (pentahelicene) formally also belong to the helicenes. The distortion of these compounds can be enhanced by proper substitution and optically stable derivatives of the latter two compounds have been obtained.[14] Pentahelicene itself proved to be sufficiently optically stable for resolution slightly below room temperature.[15]

In this paper the synthesis and properties of some heterohelicenes[16] are described. The possibility of constructing helicenes with five-membered heterocycles is obvious if we compare the geometry of benzene with thiophene, furan, and pyrrole (see Chart I).[17] Most important in this respect are the angles between the two formal carbon–carbon double bonds which can take part in the annelation to form a helicene since the sum of these angles of all fused rings is an approximate

CHART I



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[1] Preliminary communications about this subject: (a) H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, **90**, 5339 (1968); (b) H. Wynberg and M. B. Groen, *Chem. Commun.*, 964 (1969); (c) H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, **92**, 6664 (1970).

[2] The name helicenes, introduced by Newman,[3] refers to ortho-condensed aromatic hydrocarbons in which all benzene rings are angularly annelated, such as to give helically shaped molecules.

[3] (a) M. S. Newman, W. B. Lutz, and D. Lednicer, *J. Amer. Chem. Soc.*, **77**, 3420 (1955); (b) M. S. Newman and D. Lednicer, *ibid.*, **78**, 4765 (1956); (c) M. S. Newman, R. S. Darlak, and L. Tsai, *ibid.*, **89**, 6191 (1967).

[4] I. R. Mackay, J. M. Robertson, and J. G. Sime, *Chem. Commun.*, 1470 (1969).

[5] A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

[6] (a) A. Moscowitz, Ph.D. Thesis, Harvard, 1959; (b) D. D. Fitts and J. G. Kirkwood, *J. Amer. Chem. Soc.*, **77**, 4940 (1955); (c) I. Tinoco and R. W. Woody, *J. Chem. Phys.*, **40**, 160 (1969); (d) J. H. Brewster, *Top. Stereochem.*, 40 (1967).

[7] The terms right-handed and left-handed are used here to describe the helicity of the helicenes; the enantiomers with right- and left-handed helicity can best be labeled with *P* (= plus) and *M* (= minus), respectively [R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966)], which in this case is less confusing than the *R–S* labeling [R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956)].

[8] R. H. Martin and D. Bogaert-Verhogen, *Tetrahedron Lett.*, 3045 (1967).

[9] (a) M. Flammang-Barbieux, J. Nasielski, and R. H. Martin, *ibid.*, 743 (1967); (b) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *ibid.*, 3507 (1968).

[10] See, *e.g.*, F. B. Mallory, C. S. Wood, and T. J. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

[11] R. H. Martin, N. Defay, H. P. Figeys, M. Flammang-Barbieux, J. P. Cosyn, M. Gelbcke, and J. J. Schurter, *Tetrahedron*, **25**, 4985 (1969).

[12] R. H. Martin, G. Morren, and J. J. Schurter, *Tetrahedron Lett.*, 3683 (1969).

[13] R. H. Martin and M. Deblecker, *ibid.*, 3597 (1969).

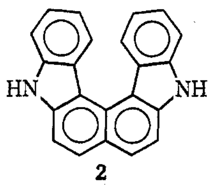
[14] See, for examples, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., and Chapman and Hall Ltd., London, 1956, Chapter 10.

[15] Ch. Goedicke and H. Stegemeyer, *Tetrahedron Lett.*, 937 (1970).

[16] We propose this name for compounds containing the helicene framework in which one or more of the benzene rings are replaced by heterocyclic rings.

[17] Data obtained from B. Bak and coworkers [*J. Mol. Spectrosc.*, **7**, 58 (1961); *ibid.*, **9**, 124 (1962); and *J. Chem. Phys.*, **24**, 720 (1956)].

measure for the overcrowding and therefore for the stability of the helix configuration. To get a full turn of a helix this sum has to be 360° as is realized in hexahelicene but which is at least in principle possible also by proper annelation of eight thiophene rings (8 × 45°). The first example of a heterohelicene was reported as early as in 1927;[18] this compound 5,10-dihydrocarbazolo[3,4-*c*]carbazole (**2**) was synthesized *via* a double Bucherer reaction. Its synthesis and properties have received renewed attention.[19] This paper deals with helicenes which contain benzene, thiophene, and/or furan rings. The synthesis of these heterohelicenes became possible by our discovery that heterocyclic analogs of stilbene upon irradiation with uv light afford the corresponding phenanthrene analogs often in high yields;[20] *e.g.*, see eq 1. Generally this synthesis involved the conversion of compounds like **4** into aldehydes and/or phosphonium salts, followed by a Wittig reaction and again a photochemical ring closure reaction. Three of the heterohelicenes described here were resolved by crystal picking. This allowed determination of optical rotatory dispersion (ORD) and circular (CD) spectra. The uv and CD spectra of heterohelicenes, which were much better resolved than those of the helicenes[21] and therefore lend themselves better for comparison of theoretical and experimental results, will be the subject of a separate paper. The racemization rates of the hexaheterohelicenes furnished insight in the optical stability of helicenes.[1b] A full structure determination of one of the hexaheterohelicenes by X-ray analysis has been published.[22]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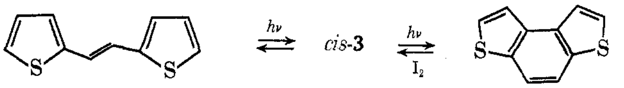
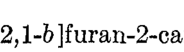


trans-**3** **4** (1)

Results

Benzo[*b*]thiophene-2-carboxaldehyde (**5**), naphtho[2,1-*b*]thiophene-2-carboxaldehyde (**6**), and naphtho[2,1-*b*]furan-2-carboxaldehyde (**7**) were prepared from the parent compounds by lithiation and subsequent formylation, as had been reported for the first of these aldehydes.[23]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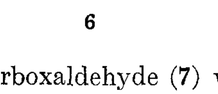
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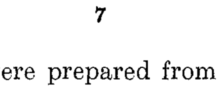
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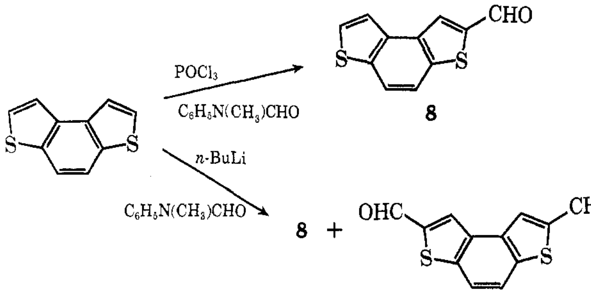
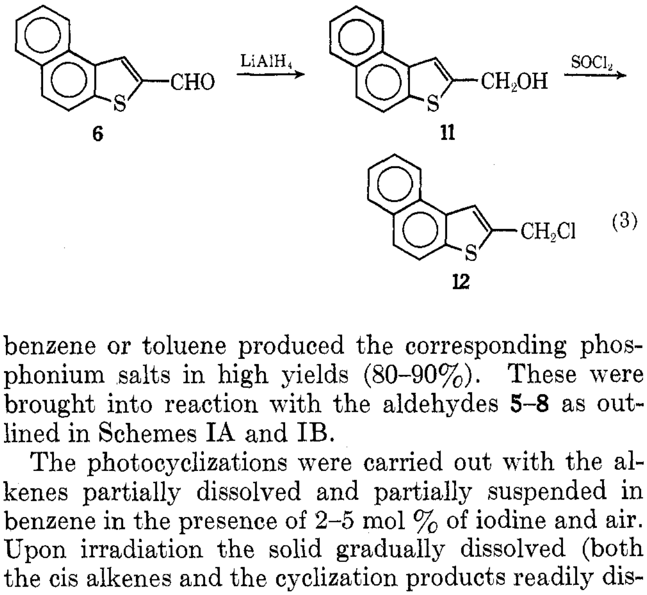
The aldehyde **6** was prepared also by a Vilsmeier reaction according to literature prescriptions.[24] Benzo[1,2-*b*:4,3-*b'*]dithiophene-2-carboxaldehyde (**8**) was obtained analogously by direct formylation or *via* lithiation (eq 2). For the Wittig condensations we needed the 2-chloromethyl derivatives of benzo[*b*]thiophene and naphtho[2,1-*b*]thiophene. Neither of these compounds can be obtained by direct chloromethylation: benzo[*b*]thiophene affords the 3-chloromethyl rather than the 2-chloromethyl derivative,[25] whereas naphtho[2,1-*b*]thiophene produces a complex mixture of products.[26] A satisfactory synthesis of 2-chloromethylbenzo[*b*]thiophene (**10**), however, has been described by Blicke and Sheets.[27] In a similar manner 2-chloromethylnaphtho[2,1-*b*]thiophene (**12**) was synthesized from the aldehyde **6** (eq 3). Although the synthesis of **12** involved three steps starting from naphtho[2,1-*b*]thiophene, the overall yield was reasonable (40%). Reaction of **10** and **12** with triphenylphosphine in refluxing benzene or toluene produced the corresponding phosphonium salts in high yields (80–90%). These were brought into reaction with the aldehydes **5**–**8** as outlined in Schemes IA and IB.



8 **9** (2)



6 **11** **12** (3)

The photocyclizations were carried out with the alkenes partially dissolved and partially suspended in benzene in the presence of 2–5 mol % of iodine and air. Upon irradiation the solid gradually dissolved (both the cis alkenes and the cyclization products readily dissolve in benzene) and eventually a clear yellow or brownish solution was formed (see Table I). At this point the irradiation was allowed to proceed for a short time and then stopped. The products were isolated

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[18] W. Fuchs and I. Niszel, *Ber.*, **60**, 279 (1927).

[19] M. Zander and W. H. Franke, *ibid.*, **102**, 2728 (1969).

[20] R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).

[21] The word helicene if it is not specified refers to a pure benzenoid helicene.

[22] G. Stulen and G. J. Visser, *Chem. Commun.*, 965 (1969).

[23] D. A. Shirley and M. J. Danzig, *J. Amer. Chem. Soc.*, **74**, 2935 (1952).

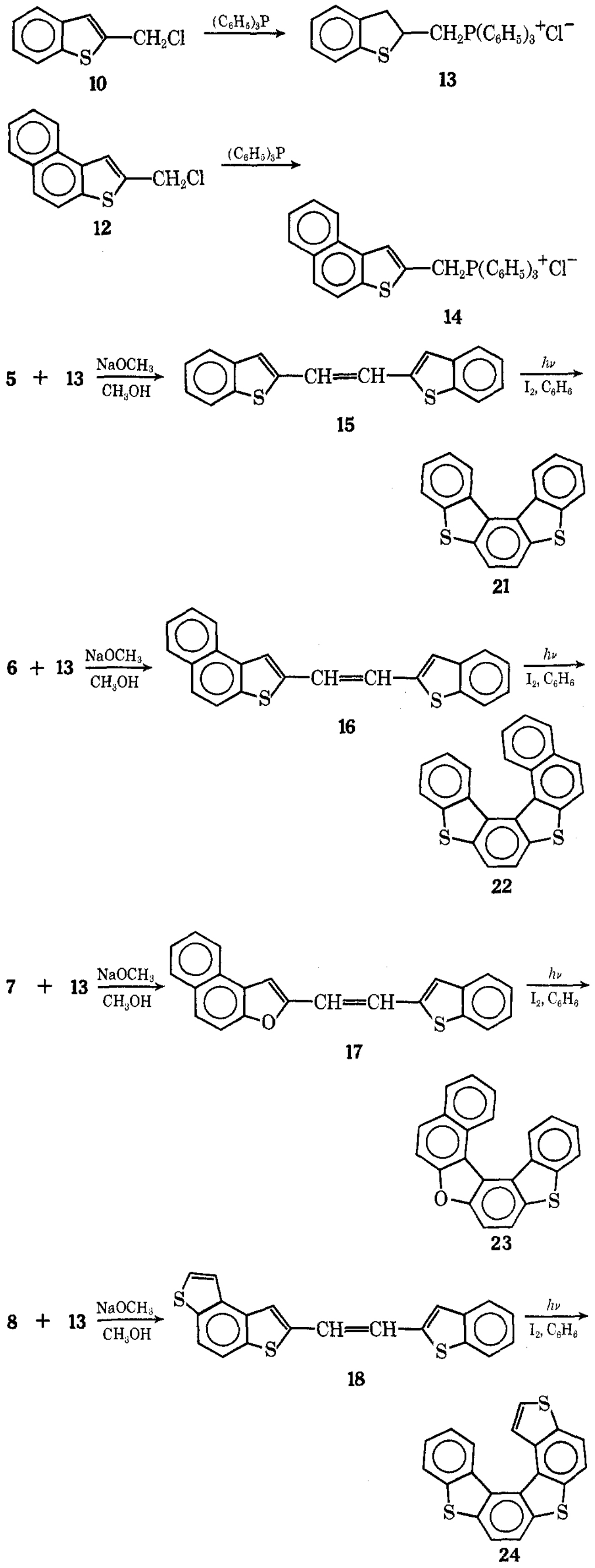
[24] K. Clarke, G. Rawson, and R. M. Scrowston, *J. Chem. Soc. C*, 537 (1969).

[25] F. F. Blicke and D. G. Sheets, *J. Amer. Chem. Soc.*, **70**, 3768 (1948).

[26] G. Rawson, private communication.

[27] F. F. Blicke and D. G. Sheets, *J. Amer. Chem. Soc.*, **71**, 2856 (1949).

SCHEME IA



SCHEME IB

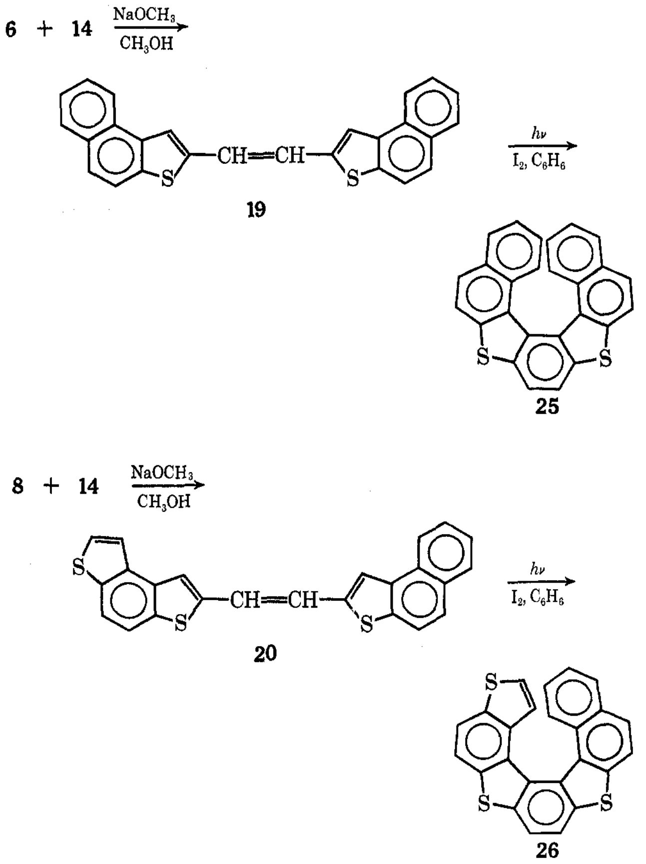


TABLE I

UV SPECTRA OF THE TRANS ALKENES (IN BENZENE)

Compd	Absorption maxima, mμ (log ε values)			
15	sh 330 (4.40)	344 (4.57)	363 (4.70)	383 (4.60)
16		363 (4.39)	382 (4.54)	405 (4.44)
17		368 (4.40)	386 (4.55)	409 (4.45)
18		359 (4.44)	379 (4.53)	402 (4.43)
19	354 (4.30)	376 (4.52)	397 (4.70)	421 (4.62)
20	354 (4.27)	378 (4.50)	399 (4.69)	423 (4.61)
28	sh 363 (4.44)	380 (4.57)	399 (4.67)	423 (4.53)
31	331 (4.36)	339 (4.39)	355 (4.41)	374 (6.64)
	399 (4.49)	420 (4.63)	446 (4.57)	

by evaporation of the solvent and column chromatography of the residue. The products fluoresce very weakly and consequently can be distinguished from the starting compounds easily. Benzo[1,2-*b*:4,3-*b'*]bis[1]-benzothiophene (**21**) is the only compound described previously;[28] it was formed from **15** in 57% yield, mp 183–185° (reported[28] 181–183°).

The hexaheterohelicene, benzo[*d*]naphtho[1,2-*d'*]-benzo[1,2-*b*:4,3-*b'*]dithiophene (**22**) was obtained from **16** in 73% yield as almost colorless needles, mp 223–225° (from benzene). The individual crystals proved to be optically active, when they were grown from a slowly evaporating benzene solution. The highest specific rotation observed (measured in $CHCl_3$ solution) was $[\alpha]^{25}_{436} = -5600°$ ($CHCl_3$). The solutions of optically active **22** racemized slowly at room temperature ($t_{1/2}$ = 4 hr at 25°). Photocyclization of **17** afforded 1-benzothieno[3,2-*e*]naphtho[2,1-*b*]benzofuran (**23**) in 40% yield. This compound, which formed colorless crystals, mp 221–222° (from benzene), was not resolved. The hexahelicene **24**, benzo[*d*]thieno[3,2-*d'*]benzo-[1,2-*b*:4,3-*b'*]bis[1]benzothiophene, obtained in 40% yield from **18**, crystallized from benzene as very pale yellow needles, mp 210–212°. Only few crystals

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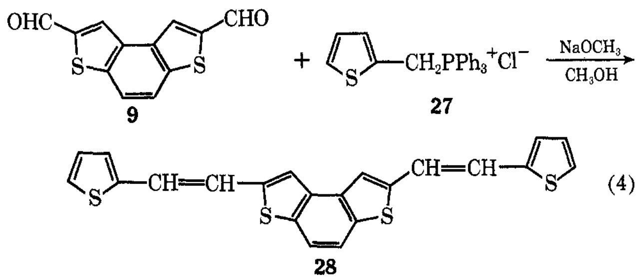
[28] D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res., Sect. B*, **17**, 260 (1958); *Chem. Abstr.*, **55**, 22282 (1961).

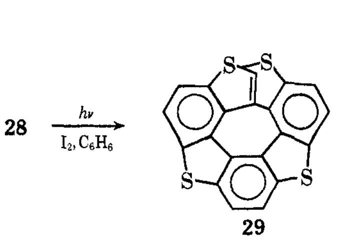
showed optical activity, but better results were obtained when the crystals were grown from a slowly evaporating toluene solution. The highest observed specific optical rotation was $[\alpha]^{25}_{436} = +3640^\circ$ (CHCl$_3$). Solutions of optically active **24** racemized rather quickly at room temperature ($t_{1/2}$ = 13 min at 25°). Irradiation of **19** furnished the heptaheterohelicene **25**, dinaphtho[1,2-*d*:1′,2′-*d*′]benzo[1,2-*b*:4,3-*b*′]dithiophene, a pale yellow compound, mp 294–297° (from benzene) in 66% yield. The crystals were racemic. The heptahelicene **26**, benzo[*e*]thieno[3,2-*e*′]benzo-[1,2-*b*:4,3-*b*′]bis[1]benzothiophene, was formed in 49% yield from **20**; it crystallized from benzene as pale yellow optically active needles, mp 216–236°. The highest specific rotation observed was $[\alpha]^{25}_{436} = +7200^\circ$ (CHCl$_3$). No racemization took place at ordinary temperature. Resolution of this compound could also be achieved by recrystallization from (−)-α-pinene. *Ca.* 50-mg quantities of **26** were dissolved with heating in 10 ml of (−)-α-pinene. The crystallized material obtained after cooling showed considerable optical activity. The optical purity of the material, which was in all cases dextrorotatory, was increased by crystallization at low temperatures.

Another approach to the synthesis of heterohelicenes similar to those described above is exemplified by the synthesis of dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]-bis[1]benzothiophene (**29**). Wittig condensation of the dialdehyde **9** and the phosphonium salt **27** afforded in high yield the orange-colored compound **28** (eq 4).



(4)

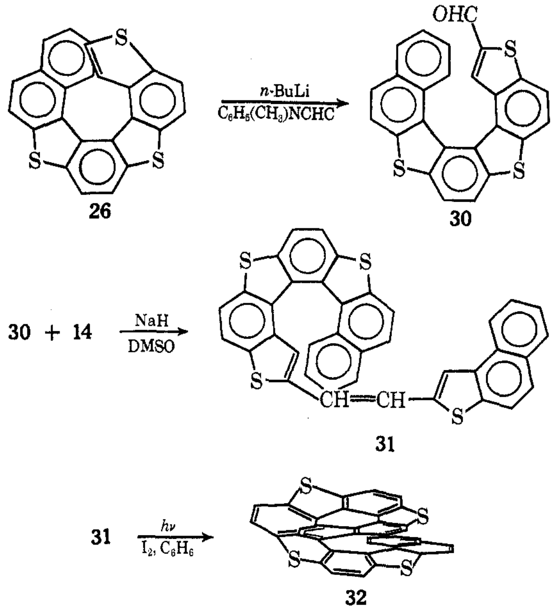
A double photocyclization reaction furnished in moderate yield the pale yellow helicene **29**, mp 269–270° (from benzene).[29] The crystals were found to be racemic (eq 5).



(5)

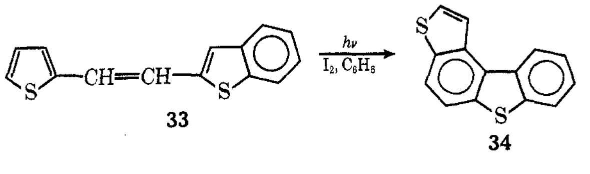
The heptahelicenes **26** and **29** have terminal thiophene rings and lend themselves for the synthesis of higher heterohelicenes. This is demonstrated in Scheme II. Lithiation of **26** and subsequent treatment with *N*-methylformanilide furnished the 2-formyl derivative **30** in 65% yield, a brilliant yellow compound, mp 243–245°. Wittig condensation of this aldehyde with **14** gave the alkene **31**, a yellow compound showing green fluorescence in solution. Since the aldehyde **30** is sparingly soluble in methanol, the Wittig reaction was carried out in dimethyl sulfoxide with sodium hydride as base. Irradiation of **31** afforded the yellow undecahelicene **32**, mp 368–370° (from benzene), in 14% yield.

SCHEME II



The reaction sequence shown in Scheme II was repeated starting with partially resolved [by recrystallization from (−)-α-pinene, see above] **26**. Thus from 15 mg of **26** with $[\alpha]^{25}_{436} = +550^\circ$ (CHCl$_3$) (optical purity *ca.* 7.5%) was obtained 1.12 mg of **32** with $[\alpha]^{25}_{546} = +270^\circ$ (CHCl$_3$). Optically pure **32** consequently must have a specific rotation of $[\alpha]^{25}_{546} = +3600^\circ$ and a molar rotation of $[\phi]^{25}_{546} = +22.000^\circ$.

Finally in order to allow comparison of the properties of the heterohelicenes with those of structurally related planar compounds, [1]benzothieno[5,4-*b*][1]benzothiophene (**34**) was synthesized according to eq 6.



(6)

The colorless product, mp 149–150°, was obtained in 73% yield.

Discussion

The Synthesis of the Aldehydes.—Metalation of thiophene and its derivatives with organolithium compounds takes place in the position adjacent to the sulfur atom (α position), if this is vacant, rather than in the β position.[30] No exception to this rule has been reported thus far, which makes this reaction a versatile tool for structure elucidation and for unambiguous syntheses. For this reason the aldehydes **5–8** initially were synthesized *via* metalation of the parent com-

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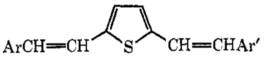
[29] The attempted double photocyclizations of compounds of the type



Ar and Ar′ = phenyl, thienyl, and/or benzo[*b*]thienyl

carried out by one of us (H. S.) were found to lead to only traces of the expected products.

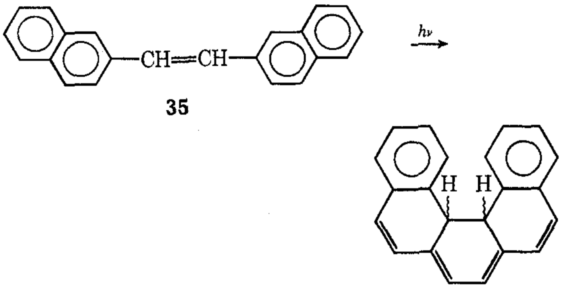
[30] See, *e.g.*, the review paper: J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

pounds. Clarke and coworkers,[24] however, in studying the electrophilic substitution of naphtho[2,1-*b*]thiophene found that in contrast to benzo[*b*]thiophene this compound is substituted preferentially in the α position and that **6** could be obtained by a Vilsmeier formylation. They attributed this to steric screening of the β position (which is the most reactive position in benzo[*b*]thiophene) by the 9 proton, similar to the peri-interaction in naphthalene. We found that analogously Vilsmeier formylation of benzo[1,2-*b*:4,3-*b'*]dithiophene (**4**) took place in the α position affording the aldehyde **8**. Although the explanation given by Clarke might be correct, we believe that the reactivity toward electrophilic substitution of the α positions of naphtho[2,1-*b*]-thiophene and of **4** is enhanced appreciably compared to the α position of benzo[*b*]thiophene, as can be seen by inspection of the resonance structures which give the major contributions to the transition state for electrophilic substitution. In accordance with this view, MO calculations carried out on this laboratory reveal that the electron density in the α position of **4** is higher and that in the β position is slightly lower than in the corresponding positions in benzo[*b*]thiophene. Interestingly enough these results resemble those obtained in the acetylation of phenanthrene,[31] the 3-substituted product being the main product.

The Wittig Reaction and Photocyclizations.—The Wittig reactions all proceeded in good yield and deserve little comment. The cis and trans structures of the resulting alkenes were assigned on the basis of the following arguments. (a) Cis isomers of stilbenes usually have a much lower melting point than the corresponding trans isomers. (b) The uv spectra of the compounds to which the trans structure was assigned showed a long wavelength band with much vibrational structure (at least four peaks with a spacing of *ca.* 1500 cm^{-1}), whereas the presumed cis isomers showed a broad structureless band. The maximum of this band was blue shifted compared to that of the trans isomer. This is a quite characteristic feature of *trans*- and *cis*-stilbene and related compounds. (c) The nmr spectra of the low melting isomers of **15** and **16** showed a singlet for the ethylene protons at τ 3.2 ppm ($CHCl_3$). This chemical shift is consistent with the cis structure only.[32] The trans alkenes were too insoluble to run nmr spectra. (d) The trans alkenes showed a highly characteristic strong absorption in the ir spectra between 930 and 940 cm^{-1}.

The mechanism of the photocyclization reactions has been discussed in a previous paper;[20] applications of this reaction and mechanistic studies have been reviewed *in extenso.*[33]

Briefly summarized the reaction involves three steps, namely, photoisomerization of the trans alkene to the cis isomer, photocyclization of the cis alkene to an intermediate of the type of 4a,4b-dihydrophenanthrene, and aromatization of this intermediate by the presence of air and a trace of iodine. A difference between the photocyclizations of thienyl- and furylethenes described previously[20] and those described here is the relatively long irradiation times which were required now, influencing the yield of cyclized product in an adverse manner.[34] This is, at least in part, due to the extremely low solubility of the trans alkenes so that slowly dissolving suspensions were irradiated. Another reason to account for the long irradiation times might be that there is an inefficient step in the photochemical process or in the aromatization of the dihydro intermediate. The latter explanation finds some precedence in the work of Timmons and coworkers[35] who found that the hindered dihydro intermediate **36** could be prepared by irradiation of a solution of 1,2-di-(naphthyl)ethene (**35**) in the presence of air (eq 7)! On the other hand low efficiency of trans to cis isomerization has also been reported in a few cases, where the cis isomers were very strained.[36]



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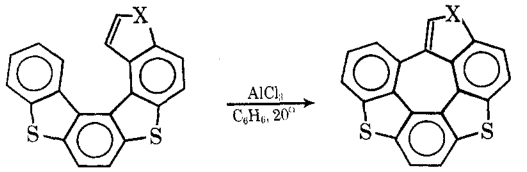
(7)

The structures of the heterohelicenes were established by spectral data (nmr, uv, mass spectra); the strongest evidence, however, is the high optical activity shown by these compounds, which is direct proof of the helicity of the molecules. Completely unambiguous is the structure proof of the hexahelicene **22** by X-ray analysis.[22] An interesting feature of the hexahelicenes **22** and **24** is the ring closure with $AlCl_3$ under extraordinarily mild conditions (eq 8). The compound **2** is reported to undergo a similar ring closure, albeit under a more drastic condition.[19] Obviously this reaction can furnish additional evidence for the structure in appropriate cases.



22, X = CH=CH
24, X = S

37, X = CH=CH
38, X = S

(8)

Resolution of the Heterohelicenes.—Racemic modifications may exist in three different types in the solid state:[37] (I) as a mechanical mixture of two types of crystals, the (+) and (−) forms (a racemic mixture or (±)-conglomerate); (II) as a racemic compound, consisting of crystals with an equal number of the enantiomeric molecules per unit cell; (III) as a racemic solid solution (pseudoracemic compound).

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[31] E. Mosettig and J. van der Kamp, *J. Amer. Chem. Soc.*, **55**, 3442 (1933).

[32] M. J. Handelé, Meeting of the Royal Dutch Chemical Society, Amsterdam, Oct 1965.

[33] (a) F. R. Stermitz, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967; (b) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

[34] In a separate experiment it was shown that the heterohelicenes decomposed slowly upon irradiation.

[35] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. C*, 163 (1970).

[36] C. Goedicke and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **73**, 782 (1969).

[37] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 31 ff.

It is very unlikely that helicenes form crystals of type III since this requires that the enantiomers are isomorphous. A simple method to resolve racemic material which can be applied only if the crystals belong to type I is separation by hand of the crystals, distinguished by their enanthiomorphous surfaces (Pasteur, 1848). It turned out that this was the case with some of the heterohelicenes, although this could not be seen from their appearance. Solutions of single crystals in chloroform, however, showed measurable optical rotations. The same method was used by Martin to get optically active samples of heptahelicene[9b] and the other helicenes, including hexahelicene.[38] In this manner we obtained the compounds **22**, **24** and **26** in optically active form. The heptaheterohelicenes **25** and **29**, however, withstood all attempts to resolution by crystal picking, the crystals obviously belonging to type II.[39] The compounds **21** and **23** were not resolved either; the former definitely cannot be sufficiently optically stable to measure any optical rotation at room temperature; the latter might be resolvable but the crystals were small and poorly developed. The specific rotations measured for the compounds **22**, **24** and **26** varied over a wide range, indicating that the crystals were not optically pure. The main reason for the optical impurity is that the large crystals used for the measurements were not really single crystals; determinations of the specific rotations with single crystals such as used in X-ray work were hampered by the small size of these crystals. A further complication arising in the resolution by crystal picking is that some compounds can exist in different modifications depending on the conditions. Recrystallization of **24**, for instance, from methylcyclohexane, furnished completely inactive crystals (type II), whereas from toluene highly active crystals were obtained. Probably temperature and impurities present can also affect the crystal modification. The resolution by hand separation is too laborious for large quantities and moreover the crystals need to be of sufficient size. Therefore other methods were looked for. Promising results were found with the recrystallization of **26** from the optically active solvent (−)-α-pinene. When the crystallization was carried out at low temperature the total amount of obtained crystals (a powder!) showed considerable optical activity. Addition of petroleum ether (bp 40–60°) to the mother liquor afforded material showing optical rotation of the opposite sign. Two explanations can be given to account for the observed results. (a) One of the enantiomers of the helicene is more readily soluble in the optically active solvent than the other, consequently the less soluble enantiomer crystallizes first. This phenomenon is thermodynamic in nature. (b) When the crystallization starts there is a good chance that a tiny nucleus of either (+) or (−) molecules is formed which inoculates the solution and causes preferential crystallization of one enantiomer. This behavior of crystallization, called spontaneous resolution, is nonthermodynamic in nature.

Arguments for the first explanation are that the crystals always showed a positive rotation and that recrystallization from toluene–petroleum ether or from methylcyclohexane did not bring about a similar resolution. Arguments for the second and against the first explanation can be raised also.

Recrystallization of **26** from (−)-α-pinene at elevated temperature, which should favor the thermodynamic process, furnished material of only low optical purity. Moreover, the nmr spectrum of **26** in (−)-α-pinene was essentially the same as in an optically inactive solvent, showing that the solvent does not strongly interact with one enantiomer selectively.[40] The heptahelicene **25**, which did not give a racemic mixture, was not resolved either upon recrystallization from (−)-α-pinene. All these facts suggest that the resolution of **26** is caused by a combination of the solubility difference and spontaneous resolution. Resolutions by crystallization from optically active solvents have been successful in very few cases.[41] Spontaneous resolution is more frequently found and it is even used for large-scale operations.

Mass Spectra.—The main features of the mass spectra of the heterohelicenes are the occurrence of doubly and even triply charged ions and the relatively few fragments with high abundance, particularly when no terminal thiophene rings are present. Generally speaking the main modes of fragmentation are loss of hydrogen, CH_3, C_2H_4, $H_2S + H_2$, CHS, and CH_3S. The abundances of the resulting fragments relative to the parent peaks (M^+) are represented in Table II.

TABLE II

MASS SPECTRA OF THE HEXA- AND HEPTAHETEROHELICENES[a]

Fragment lost from M^+	**22**	**24**	**25**	**26**	**29**	**23**
H	45	90	10.5	11	4.6	31
H_2	47	72	13	5.5	4.8	35
H_4	12		9.2	5.5		
CH_3	10	1.5	2.1	1.5	3.3	5.4
C_2H_4			9.6	16.7	3.8	
H_2S		3.8	4.9	13.4	24	
H_4S		2.3	2.0		3.8	
CHS		4.3	9.6	2.4	4.2	
CH_3S		10	4.9	10	15	
C_3H_5			7.5			
CHO						7.5
CH_3O						5.6

[a] Relative abundances, $M^+ = 100$.

In Table II the fragments due to the C_{13} and S_{34} isotopes (mainly the strong $M + 1$ and $M + 2$ peaks) have been omitted as well as fragments with mass $m \leqslant M/2$ or with an abundance *ca.* 2%. From the table it can be seen that loss of hydrogen is the most important fragmentation of the hexahelicenes. This is undoubtedly the result of the favorable geometry of these compounds, giving rise to a process analogous to the ring closure with $AlCl_3$ (see eq 8). The loss of CH_3 is less readily explained since it requires a drastic rearrangement of the molecule.

An interesting phenomenon is that the heptaheterohelicenes but not the hexaheterohelicenes lose C_2H_4. It is known that hexahelicene (**1**) undergoes rearrangement to the stable planar coronene very efficiently in

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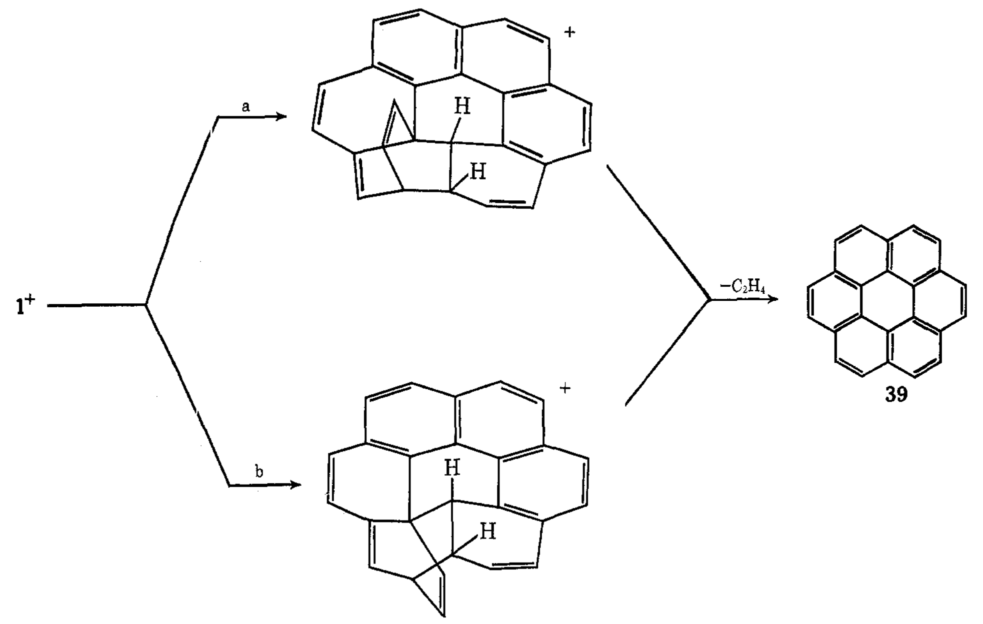
[38] R. Martin, private communication.

[39] This was confirmed for **29** by X-ray analysis, which showed that the crystals belong to a centrosymmetric space group (G. J. Visser, private communication).

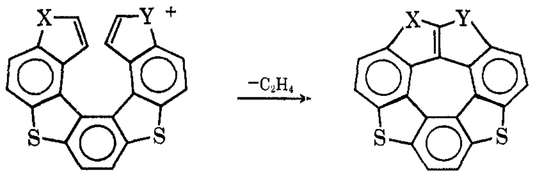
[40] Examples of enantiomers showing nonequivalent nmr spectra in appropriate optically active solvents have been reported: W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *Tetrahedron Lett.*, 5489 (1968).

[41] (a) R. M. Secor, *Chem. Rev.*, **63**, 297 (1963); (b) D. R. Buss and T. Vermeulen, *Ind. Eng. Chem.*, **60** (8), 12 (1968).

the mass spectrometer with loss of C_2H_4. This has been studied extensively by Dougherty, who suggested a Diels–Alder type reaction between the terminal benzene rings (eq 9).[42] From theoretical and experimental evidence this author favored path a, although *a priori* path b seems more likely since it requires a less strained intermediate. A reaction similar to that of hexahelicene (**1**) would in the case of the hexaheterohelicenes produce very strained molecules, but in the case of the heptaheterohelicenes appreciable deviations of the normal bond lengths and angles are not necessary. Therefore we propose that the following process takes place (eq 10).



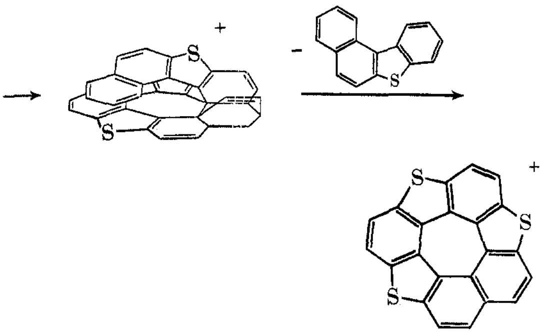
39 (9)



(10)

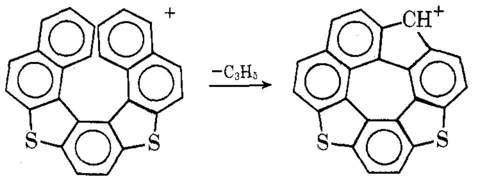
25, X = Y = CH═CH **40**, X = Y = CH═CH
26, X = S; Y = CH═CH **41**, X = S; Y = CH═CH
29, X = Y = S **42**, X = Y = S

Substantial evidence for the proposed rearrangement is given by the mass spectrum of the undecahelicene **32**, which besides numerous fragments in low abundance (<10%) shows as the main fragment m/e 368 (abundance 25% relative to M^{+}). This is no doubt again[41] formed according to eq 11.

32 →


(11)

A metastable peak at m/e 226 belonging to the fragmentation 602 → 368 can also be seen, which suggests that the formation of **41** from the intermediate occurs in a single step. There is, however, no indication in the mass spectrum for the presence of benzo[*b*]naphtho[1,2-*d*]thiophene which would provide direct evidence for a path a reaction. The fragments H_2S and CH_3S apparently originate predominantly from terminal thiophene rings, whereas CHS is also lost from compounds with thiophene completely fused. This is not unique and has been reported in the literature.[43] C_3H_5 is lost in only one case and probably the formation of a stable planar ion is again the driving force (eq 12). The same fragmentation pattern as pictured here was observed with the doubly charged ions, although the relative abundances were different.



25 **42** (12)

Nmr Spectra.—The protons in the heterohelicenes, starting with benzo[1,2-*b*:4,3-*b'*]dithiophene can be divided in two groups, those attached to the terminal rings and those along the outer periphery. Of these periphery protons those which are closest to the middle of the molecule usually are at the lowest field. They move slowly to lower field on progressive annelation [they obey almost exactly the rule $\tau = 153 - 5n$ (cps), where n is the number of rings]. The other periphery protons are at a higher field, probably due to normal ring current effects. The protons of the terminal rings show the most interesting behavior, since in the compounds containing four or five aromatic rings these protons are in the deshielding zone of the opposite ring, assuming that the terminal rings are almost coplanar. Therefore these protons are found at low field, in particular the protons in the angular positions. On further

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[42] R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 3788 (1968).

[43] S. Meyerson and E. K. Fields, *J. Org. Chem.*, **33**, 847 (1968).

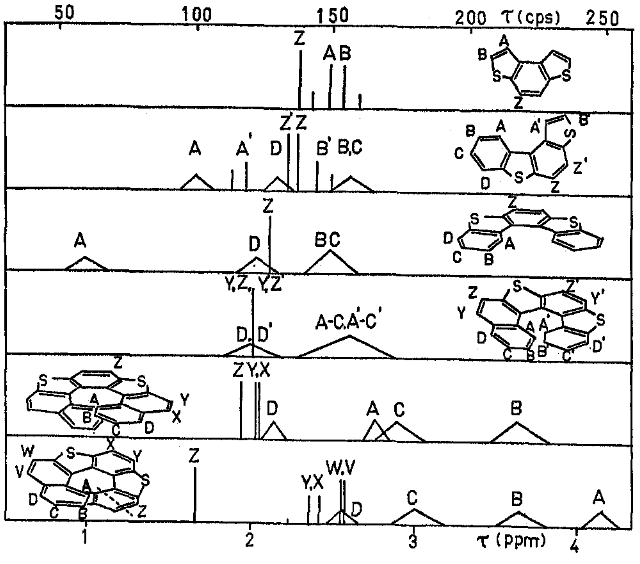

Figure 1.—Diagrammatic representation of the nmr spectra of a number of heterohelicenes (CDCl$_3$, 60 MHz).

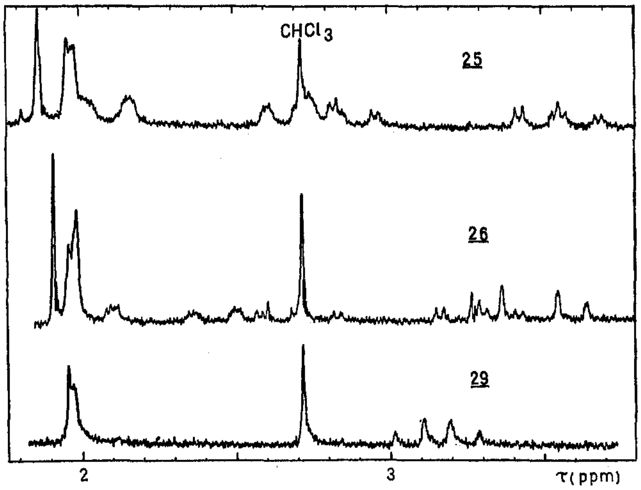

Figure 2.—The nmr spectra of the heptaheterohelicenes (CDCl$_3$, 60 MHz).

annelation, however, the compounds become helical and some of the protons in the terminal rings are moved into the shielding zone of the underlying benzene or thiophene ring. These protons appear now at unusually high field. The results are represented in Figure 1.

The periphery protons form a series of two-spin systems, each giving in principle a singlet (A_2 system) or two doublets (AB system with $J = 9$ cps). The real pattern is simplified because of the C_2 symmetry or quasi-C_2 symmetry (caused by the resemblance between thiophene and benzene) and the often fortuitously coinciding signals. A terminal thiophene ring gives an AB pattern (with $J = 5$–6 cps) and unambiguous assignment is possible by lithiation and deuteration. Terminal benzene rings give more difficulties, since we have now one or two four-spin systems. The protons having two neighboring protons (B and C in Figure 1) can be distinguished from those having one (A and D) if there is not too much overlap of the signals, since the ortho coupling (7–9 cps) is large compared with the meta and para coupling (*ca.* 1.5 and 05 cps, respectively). Consequently, the signals for A and B are

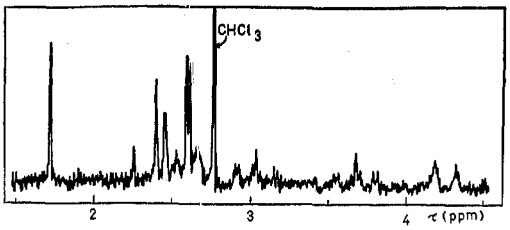

Figure 3.—The nmr spectrum of the undecaheterohelicene (CDCl$_3$, 60 MHz).

roughly doublets and for B and C triplets. Further assignments were made by considering the geometry of the molecule and by comparison with the nmr spectra of the helicenes analyzed in detail by Martin and coworkers (computer simulation).[11] The nmr spectra of the heptaheterohelicenes are shown in Figure 2 and that of the undecahelicene **32** in Figure 3.

Experimental Section

Photolyses were carried out with a Hanau Q-700 or with a smaller Hanau S-81 unfiltered high-pressure mercury lamp. About 500–600 ml of solution could be irradiated with the Q-700 and 100–130 ml with the S-81 lamp. The spectral distribution of these lamps is almost identical (virtually a continuous spectrum with maxima at 366 and 313 mμ) but the Q-700 lamp is a factor 5 more intense than the S-81 lamp. The irradiations were carried out usually at room temperature. Both the Q-700 and S-81 lamp are of the immersion type.

Melting points up to 340° were determined on a Reichert hot stage apparatus and are uncorrected. Melting points above 340° were determined in a copper melting point block, heated with a flame. In these cases a stem correction was applied to the observed melting points. Boiling points are uncorrected. Nmr spectra were obtained with a Varian A-60 using tetramethylsilane as an internal standard. The chemical shifts are expressed in parts per million on the τ scale. Ultraviolet spectra were determined with a Zeiss PMQ II or recorded with a Beckman DB-G grating spectrophotometer. Mass spectra were obtained with an AEI MS902 instrument. Gas chromatography was done with a F & M Model 819 gas chromatograph. Merck alumina neutral, activity I, was used for column chromatography and in an exceptional case silica gel (BDH). Elemental analyses were carried out by the microanalytical department of this laboratory under supervision of Mr. W. M. Hazenberg.

Benzo[*b*]thiophene-2-carboxaldehyde (**5**).—This compound was prepared according to the literature[23] from benzo[*b*]thiophene *via* lithiation and reaction with *N*-methylformanilide. The product was obtained in 42% yield and had mp 32.5–33° (lit.[23] 62%, mp 34–34.5°).

Naphtho[2,1-*b*]thiophene-2-carboxaldehyde (**6**). **A.** ***Via* the Vilsmeier Reaction.**—In a flask 4.6 g (0.0250 mol) of naphtho[2,1-*b*]thiophene,[44] 4.4 g (0.028 mol) of POCl$_3$, and 3.8 g (0.028 mol) of *N*-methylformanilide were combined. The magnetically stirred mixture was gradually heated on a water bath to 80° and kept at that temperature for 45 min. The dark reaction mixture was taken up in chloroform and this solution was washed with sodium acetate solution, dilute hydrochloric acid, and sodium bicarbonate solution. The chloroform solution was dried over anhydrous K$_2$CO$_3$ and the solvent was evaporated. The residue was redissolved in ether and treated with decolorizing carbon. The solution was filtered and the solvent evaporated. After recrystallization from ethanol 3.3 g (0.0156 mol, 62%) of slightly yellow **6** was obtained, mp 119.5–122.5° (lit.[24] 65%, mp 119–121°). Recrystallization from benzene furnished a less colored product.

B. ***Via* Lithiation.**—In a three-necked flask was put 2.4 g (0.013 mol) of naphtho[2,1-*b*]thiophene[44] and 10 ml of dry ether. The flask was equipped with a reflux condenser, a dropping funnel, and a gas inlet tube. The solution was kept under a nitrogen atmosphere and 25 ml of *n*-butyllithium solution (*ca.* 1 *N* in ether) was added. The solution was refluxed on a water

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[44] J. E. Banfield, W. Davies, B. C. Ennis, S. Middleton, and Q. N. Porter, *J. Chem. Soc.*, 2603 (1956).

bath for 1 hr; 3.3 g (0.024 mol) of *N*-methylformanilide in 5 ml of ether was added dropwise to the magnetically stirred solution. The reaction mixture was refluxed (20 min), cooled, and poured into excess of 2 *N* hydrochloric acid. The aqueous layer was separated from the organic layer and extracted with ether (50 ml). The combined ether layers were washed with water and sodium bicarbonate solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was shaken with 50 ml of a saturated sodium bisulfite solution. The precipitate was collected by filtration, washed with ether, dried, and shaken with 100 ml of 10% sodium carbonate solution and 100 ml of ether. The ether layer was dried (anhydrous $MgSO_4$). Evaporation of the solvent left a pale yellow residue, which was recrystallized from ethanol. The yield of pure **6** was 0.8 g (29%), mp 118–120°. The compound was identical with that obtained *via* the Vilsmeier reaction (mixture melting point, spectral data).

Naphtho[2,1-*b*]furan-2-carboxaldehyde (7).—In a three-necked flask was put 1.0 g (6.0 mmol) of naphtho[2,1-*b*]furan[45] and 90 ml of dry ether. This solution was kept under a dry nitrogen atmosphere and 5 ml of *n*-butyllithium in hexane (2 *N*, 0.01 mol) was added. The magnetically stirred reaction mixture was allowed to reflux for 10 min. After cooling a solution of 1.5 g of dimethylformamide (0.02 mol) in 10 ml of ether was added over a period of 10 min. After refluxing for 0.5 hr the reaction mixture was poured on a mixture of crushed ice and 2 *N* hydrochloric acid (50 ml). The organic layer was separated and the aqueous layer was extracted twice with 50 ml of ether. The combined organic layers were washed with water and sodium bicarbonate solution and dried over $NaSO_4$. After evaporation of the solvent a brown oil was obtained which was purified by column chromatography over silica gel with ether as eluent. The product, which solidified after standing some time in the refrigerator, was obtained in 45% yield (0.52 g, 2.7 mmol) and had mp 76–77°; nmr spectrum (hexadeuterioacetone) singlets at τ 0.06 (1 H, aldehyde proton) and 1.64 (1 H, furan proton), unresolved multiplet between 1.6 and 2.5 ppm (4 H, benzene protons).

Anal. Calcd for $C_{13}H_8O_2$: C, 79.59; H, 4.11. Found: C, 79.5, 79.6; H, 4.0, 4.1.

Benzo[1,2-*b*:4,3-*b'*]dithiophene-2-carboxaldehyde (8). A. *Via* Vilsmeier Formylation.—In a flask were put 0.95 g (5.0 mmol) of benzo[1,2-*b*:4,3-*b'*]dithiophene[20] (**4**), 0.97 g (6.3 mmol) of *N*-methylformanilide, and 3 ml of toluene. The magnetically stirred mixture was heated on a water bath for 3 hr maintaining the temperature between 75 and 95°. The hot reaction mixture was poured in a sodium acetate solution in a 250-ml beaker, 50 ml of ether was added, and the whole mixture was transferred to a separatory funnel. The ether layer was washed with dilute hydrochloric acid, water, and sodium bicarbonate solution. After drying (anhydrous $MgSO_4$) the ether was evaporated and the residue chromatographed over silica gel. Elution with benzene furnished 0.29 g (30%) of starting material and elution with chloroform gave the aldehyde, which was recrystallized from methanol, yield 0.56 g (51% based on the total amount of **4**, 74% on not recovered **4**) of pale yellow aldehyde, mp 102–103°.

B. *Via* Lithiation.[4]—In a three-necked flask were placed 1.9 g (10 mmol) of benzo[1,2-*b*:4,3-*b'*]dithiophene and 80 ml of dry ether. The flask was equipped with a reflux condenser, a dropping funnel, and gas inlet tube. The solution was brought under a dry nitrogen atmosphere. Through the condenser 5 ml of *n*-butyllithium (2.3 *N* in hexane, 11.5 mmol) was added with a pipet. The resulting mixture was stirred magnetically at room temperature for 15 min. Subsequently 1.7 g (12.5 mmol) of *N*-methylformanilide in 5 ml of dry ether was added dropwise with stirring. The reaction mixture was stirred for another 10 min at room temperature and then poured in an excess of 2 *N* hydrochloric acid. Some precipitate was formed and removed by filtration. Recrystallization from acetone yielded 60 mg of pale yellow dialdehyde (3%). The organic layer was washed with water and sodium bicarbonate solution. After drying over anhydrous $MgSO_4$ the solvent was evaporated, to leave an oily residue. Chromatography over silica gel with benzene yielded 0.14 g of starting material (7%), whereas with chloroform the product was eluted. The crude product was obtained in 54% yield, based on unrecovered starting material. After recrystallization 0.77 g (40% on not recovered **4**) of pure **8** was obtained: mp 102–103°; nmr spectrum ($CDCl_3$) singlets at τ −0.03 (1 H, aldehyde proton), 1.82 (1 H, thiophene proton), 2.38 (2 H, thiophene protons unsubstituted ring), and two doublets (J = 9 cps) centered at τ 2.17 and 2.28 ppm (2 H, benzene protons).

Anal. Calcd for $C_{11}H_6OS_2$: C, 60.52; H, 2.77; S, 29.38. Found: C, 60.5, 60.3; H, 2.8, 2.8; S, 29.1, 29.3.

Benzo[1,2-*b*:4,3-*b'*]dithiophene-2,7-dicarboxaldehyde (9).—To a solution of 1.0 g (5.2 mmol) of **4** in 100 ml of dry ether, which was kept under a dry nitrogen atmosphere, was added 10 ml of *n*-butyllithium (2 *N* solution in hexane) (20 mmol). The mixture was allowed to reflux for 0.5 hr. A dark somewhat turbid solution was obtained. Excess of dimethylformamide (7.0 g, 0.1 mol) in 10 ml of dry ether was added in a few minutes and the resulting mixture was allowed to reflux for 0.5 hr. The reaction mixture was poured into a mixture of 30 ml of 2 *N* hydrochloric acid and 100 g of ice–water. A precipitate of the dialdehyde was formed, which was filtered off and dried. The yield of the crude product was 1.28 g (5.2 mmol, 99%). Attempts to recrystallize the compound failed, because of its high insolubility in ordinary solvents. The product could be purified by sublimation but only 0.30 g (22%) was obtained, since appreciable carbonizing took place. The pure yellow product did not melt but decomposed with charring at 252°: nmr spectrum (CD_3SOCD_3) singlets at τ −0.55, 0.57, and 1.25 ppm.

Anal. Calcd for $C_{12}H_6O_2S_2$: C, 58.52; H, 2.36; S, 26.04. Found: C, 58.4, 58.3; H, 2.6, 2.6; S, 25.8, 25.7.

2-Hydroxymethylnaphtho[2,1-*b*]thiophene (11).—To a suspension of 2.0 g (0.052 mol) of lithium aluminum hydride in 100 ml of dry ether in a 1-l. three-necked flask, fitted with reflux condenser and dropping funnel, was added dropwise with vigorous magnetic stirring and with external cooling by an ice bath a solution of 3.75 g (0.017 mol) of naphtho[2,1-*b*]thiophene-2-carboxaldehyde (**6**) in 375 ml of dry ether. After the addition was complete (30 min) the reaction mixture was refluxed for 30 min. The flask was cooled in an ice bath and water was added dropwise (carefully!) with vigorous stirring until a sticky mass had been formed and no further reaction was observed. Then 30 ml of concentrated hydrochloric acid was added, which resulted in a clear solution. The ether layer was separated and washed with water and sodium bicarbonate solution. After drying over anhydrous $MgSO_4$ the ether was evaporated, leaving a colorless solid, which was recrystallized from carbon tetrachloride. The yield of carbinol was 3.5 g (93%): mp 105–106.5°; nmr spectrum ($CDCl_3$) broadened singlets at τ 5.08 (2 H, CH_2OH) and 7.75 (1 H, CH_2OH), complex pattern between τ 1.75 and 2.65 ppm (7 H, aromatic protons).

Anal. Calcd for $C_{13}H_{10}OS$: C, 72.8; H, 4.71; S, 14.96. Found: C, 72.2, 72.3; H, 4.6, 4.8; S, 14.9, 15.0.

2-Chloromethylnaphtho[2,1-*b*]thiophene (12).—Carbinol **11** (3.5 g, 0.0163 mol) was mixed with 10 ml of freshly distilled thionyl chloride, which caused a vigorous evolution of SO_2 and HCl. A reflux condenser was attached to the flask, which subsequently was heated on a water bath at 80° for 10 min. The excess of thionyl chloride was removed *in vacuo* and the residue was taken up in benzene. The benzene solution was washed with sodium bicarbonate solution several times until no CO_2 evolution took place anymore. After drying over anhydrous $MgSO_4$, the benzene solution was treated with decolorizing carbon. Filtration and evaporation of solvent *in vacuo* left a colorless solid, which was recrystallized from carbon tetrachloride. The yield was 3.2 g (84%): mp 133–135°; nmr spectrum ($CDCl_3$) broad singlets at τ 2.17 (1 H, thiophene proton), 2.30 (2 H, bridge protons), and 5.10 (2 H, CH_2Cl), complex pattern between τ 1.75 and 2.65 ppm (4 H, protons terminal benzene ring).

Anal. Calcd for $C_{13}H_9CS$: C, 67.09; H, 3.90; S, 13.78. Found: C, 67.0, 67.3; H, 3.9, 3.9; S, 13.8, 13.7.

2-Triphenylphosphoniomethylbenzo[*b*]thiophene Chloride (13).—A solution of 10.5 g (0.040 mol) of triphenylphosphine and 6.8 g of 2-chloromethylbenzo[*b*]thiophene (**10**) in 20 ml of benzene was refluxed with magnetic stirring for 17 hr. The precipitate of the phosphonium salt was collected by filtration and washed with benzene. After drying, 11.5 g (0.026 mol, 70%) of **13**, mp 262–266° dec, was obtained. The filtrate was concentrated to a volume of *ca.* 6 ml and was allowed to reflux for 6 hr. This yielded a second crop of product, 2.9 g (0.006 mol, 18%).

2-Triphenylphosphoniomethylnaphtho[2,1-*b*]thiophene Chloride (14).—A solution of 2.8 g (0.0120 mol) of 2-chloromethylnaphtho[2,1-*b*]thiophene (**12**) and 3.4 g (0.0131 mol) of triphenyl-

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[45] Y. K. Yurév and D. Eckhardt, *Zh. Obshch. Khim.*, **31**, 3526 (1961).

phosphine in 10 ml of toluene was refluxed with stirring for 11 hr. The precipitate was collected on a Büchner funnel and washed with acetone. The pure product weighed 5.0 g (0.101 mol, 84%) and had mp 268–272° dec.

General Procedure for the Wittig Reactions.—The Wittig reactions were generally carried out by dissolving equimolar amounts of the appropriate aldehyde and the appropriate phosphonium salt in dry methanol (3–5 ml/mmol), if necessary with slight heating, in a flask fitted with a reflux condenser. The solution was stirred vigorously (magnetic stirrer) and through the condenser was added dropwise from a graduated pipet a solution of sodium methoxide in dry methanol over a period of 5–10 min. Usually double the theoretical amount of base was added. To complete the reaction the mixture was allowed to reflux for 0.5–1 hr. In all cases the yellow product precipitated and was filtered with suction on a sintered glass funnel, washed with methanol, and dried in an oven. The crude products, formed in almost quantitative yields, were immediately used for the photocyclization reactions. To obtain analytical pure samples the extremely insoluble trans alkenes were separated from the more readily soluble cis isomers. The trans alkenes were purified further by sublimation *in vacuo*. No attempts were made to obtain completely pure cis isomers. The trans alkenes are yellow high-melting compounds, which in solution show blue fluorescence.

General Procedure for the Photocyclization Reactions.—The conditions for the photocyclization reactions were much the same as described previously for the dithienylethenes[20] except that because of the insolubility of the trans alkenes suspensions rather than solutions were used. Either 100–200 mg of alkene in 120–130 ml of benzene was irradiated with a S-81 lamp, or *ca.* 500 mg in 550 ml of benzene with a Q-700 lamp. A crystal of iodine was added (2–5 mol % with respect to the starting material). The irradiations were carried out under air at 20–30°, without use of a filter, unless otherwise stated. During the irradiations the starting material slowly dissolved and eventually a clear solution was obtained. At this point the irradiation was continued for 0.5–1 hr and then stopped. The solvent was evaporated *in vacuo* leaving a brown residue, which was chromatographed over alumina (a column of approximately 20 × 1.5 cm was used) with benzene as eluent. The products, which are very weakly fluorescent, could easily be distinguished on the column from the strongly fluorescent trans alkenes (200 ml of benzene was sufficient to elute the product). The trans alkene, if present, stayed at the top of the column as did some tarry side products. From the eluate the cyclization product was obtained in fairly pure state, the only impurity being biphenyl. To remove this the powdered product was stirred with petroleum ether, and after the highly insoluble helicene had settled the liquid was removed with a pipet. Further purification was accomplished by recrystallization from benzene or a benzene–petroleum ether mixture. The results described below are of typical runs and are not all optimal.

1,2-Di-(2-benzo[*b*]thienyl)ethene (15).—A solution of 4.5 g (10 mmol) of the phosphonium salt **13** and 1.62 g (10 mmol) of the aldehyde **5** were mixed with 7 ml of dry methanol. A reflux condenser was attached to the flask. To the magnetically stirred solution was added at room temperature 6 ml of 2 *N* sodium methoxide solution in methanol from a graduated pipet. During the addition, which took *ca.* 10 min, a thick yellow precipitate of the product was formed, which prevented efficient stirring. For this reason 20 ml of dry methanol was added. The reaction mixture was allowed to reflux for 45 min. After cooling the precipitate was filtered with suction, washed with a little methanol, and dried. The crude product (3.0 g) was treated with 100 ml of hot benzene and the mixture was filtered. The trans isomer remained on the filter (1.45 g, 50 mmol, 50%), whereas evaporation of the solvent from the filtrate and recrystallization of the residue from benzene–petroleum ether yielded 1.0 g (34 mmol, 34%) of the yellow cis isomer, mp 130–133°, which contained only a trace of *trans*-**15**.

In order to obtain an analytically pure sample, 0.24 g of *trans*-**15** was dissolved in 100 ml of hot benzene. The solution was filtered and cooled to 25°. The precipitate, collected by filtration, consisted of brilliant pale yellow leaflets, with mp 300–301°. A yield of 0.19 g was obtained, which indicates that the solubility of *trans*-**15** in benzene is not more than 0.5 g/l. at 25°.

Anal. Calcd for $C_{18}H_{12}S_2$: C, 73.93; H, 4.14; S, 21.93. Found: C, 73 5, 73.4; H, 4.0, 4.1; S, 21.6, 21.8.

Benzo[1,2-*b*:4,3-*b'*]bis[1]benzothiophene (21).—A suspension of 200 mg of *trans*-**15** in 130 ml of benzene, to which 5 mg of iodine had been added, was irradiated with a S-81 lamp at 20–25°. After 1.5 hr a homogeneous solution had been formed and after 3 hr the irradiation was stopped. The solvent was evaporated and the residue chromatographed over alumina with benzene. A colorless product was obtained, which was recrystallized from benzene–petroleum ether (bp 40–60°), 1:1. The yield of **21** was 112 mg (57%), mp 183–185° (lit.[28] 181–183°).

1-(2-Benzo[*b*]thienyl)-2-(2-naphtho[2,1-*b*]thienyl)ethene (16).—In 4 ml of dry methanol in a 25-ml flask were dissolved 212 mg (1.0 mmol) of the aldehyde **6** and 445 mg (1.0 mmol) of the phosphonium salt **13**, by magnetic stirring and slight heating. A reflux condenser was attached to the flask and through the condenser was added dropwise in 5 min 2 ml of 2 *N* $NaOCH_3$ in dry methanol (4 mmol), with vigorous stirring. The mixture was allowed to reflux for 1 hr, cooled, and filtered with suction. The yellow product was washed with methanol, water, and again with some methanol. After drying 320 mg (0.93 mmol, 93%) of crude product was obtained, which was used for the photocyclization without further purification. Separation in the cis and trans isomer was achieved by recrystallization from 90 ml of benzene, which afforded 157 mg (46%) of pure *trans*-**16**, mp 297–298°. Partial evaporation of the solvent produced a precipitate of 30 mg (9%) of the trans compound, whereas evaporation to dryness and recrystallization of the residue from petroleum ether (bp 60–80°)–chloroform yielded 90 mg (26%) of the impure cis isomer, mp 153–155°. An analytically pure sample of *trans*-**16** was prepared by sublimation *in vacuo*.

Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.16; H, 4.12; S, 18.72. Found: C, 76.9, 77.1; H, 4.2, 4.2; S, 18.8, 18.6.

Benzo[*d*]naphtho[1,2-*d*]benzo[1,2-*b*:4,3-*b'*]dithiophene (22).—A suspension of 160 mg of **16** in 120 ml of benzene, to which 10 mg of I_2 was added, was irradiated with a S-81 lamp (Vycor filter) at 30° during 16 hr. The solvent was evaporated and the residue chromatographed over alumina with benzene. Evaporation of the collected fractions left an almost colorless material, which was purified according to the general procedure. The yield of **22** was 117 mg (73%), mp 223–225° (from benzene).

Anal. Calcd for $C_{22}H_{12}S_2$: C, 77.60; H, 3.56; S, 18.84. Found: C, 77.2, 77.3; H, 3.7, 3.7; S, 18.8, 19.0.

1-(Naphtho[2,1-*b*]furan-2-yl)-2-(benzo[*b*]thien-2-yl)ethene (17).—To a solution of 196 mg (1 mmol) of the aldehyde **6** and 446 mg (1 mmol) of the phosphonium salt **13** in 15 ml of dry methanol was added with stirring 2 ml of 1 *N* $NaOCH_3$ solution in methanol (2 mmol). The reaction mixture was allowed to reflux for 0.5 hr and subsequently cooled in an ice bath. The yellow precipitate, which had been formed, was collected by filtration and dried. The yield of the crude product was 287 mg (90%), mp 240–243° (after sublimation).

Anal. Calcd for $C_{22}H_{14}OS$: C, 80.96; H, 4.33; S, 9.83. Found: C, 80.6, 80.7; H, 4.3, 4.4; S, 9.5, 9.5.

Naphtho[2,1-*b*][1]benzothieno[3,2-*e*]benzofuran (23).—A solution of 200 mg of the alkene **17** and a trace of iodine in 0.55 l. of benzene was irradiated with a Q-700 lamp for 6 hr. The solution was concentrated and chromatographed over alumina with benzene. Evaporation of the collected fractions left a colorless product, which was washed with pentane as described in the general procedure. The yield of **23** was 80 mg (40%), mp 221–222°.

Anal. Calcd for $C_{22}H_{12}OS$: C, 81.46; H, 3.73; S, 9.84. Found: C, 81.0, 81.1; H, 3.8, 4.0; S, 9.8, 9.9.

2-[β-(2-Benzo[*b*]thienyl)vinyl]benzo[1,2-*b*:4,3-*b'*]dithiophene (18).—In 10 ml of dry methanol in a 25-ml flask were dissolved 400 mg (1.84 mmol) of aldehyde **8** and 840 mg (1.89 mmol) of the phosphonium salt **13** with stirring and slight heating. Through the reflux condenser was added 4 ml of 1.2 *N* $NaOCH_3$ in CH_3OH in 5 min with vigorous stirring. The reaction mixture was allowed to reflux (30 min). After cooling the yellow precipitate was filtered with suction, washed with some methanol, and dried. The yield of crude product was 700 mg. The product was dissolved in hot toluene, the solution was filtered, and part of the solvent was evaporated *in vacuo*. After cooling the preipitated trans isomer was collected by filtration and dried *in vacuo*. The yield of pure *trans*-**18** was 375 mg (1.08 mmol, 59%), mp 289–293°. Evaporation of the filtrate to almost dryness and addition of petroleum ether gave 150 mg (0.43 mmol, 23%) of a mixture of *cis*- and *trans*-**18**. An analytically pure sample of *trans*-**18** was obtained by sublimation *in vacuo*.

Anal. Calcd for $C_{20}H_{12}S_3$: C, 68.93; H, 3.48. Found: C, 69.4, 69.3; H, 3.7, 3.8.

Thieno[3,2-*d*]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (24).—In 120 ml of benzene was suspended 100 mg of **18** (the crude product). A small crystal (5 mg) of iodine was added and the mixture was irradiated with a S-81 lamp at 30°. After 2 hr a clear solution was obtained and after 3.5 hr the irradiation was stopped. The solvent was evaporated and the residue chromatographed over alumina with benzene. Evaporation of the collected fractions left an almost colorless material, which was purified as usual. The yield of **24** was 40 mg (40%), mp 210–212° (from benzene).

Anal. Calcd for $C_{20}H_{10}S_3$: C, 69.23; H, 2.91; S, 27.76. Found: C, 69.4, 69.6; H, 2.9, 3.0; S, 27.6, 27.9.

1,2-Di-(2-naphtho[2,1-*b*]thienyl)ethene (19).—In 40 ml of dry methanol in a 100-ml flask were dissolved 0.636 g (3.0 mmol) of the aldehyde **6** and 1.50 g (3.0 mmol) of the phosphonium salt **14** with slight heating and stirring. Through the reflux condenser was added dropwise in 5 min 6 ml of 1.0 *N* $NaOCH_3$ in CH_3OH with vigorous stirring. The reaction mixture was allowed to reflux for 30 min and cooled, and the yellow precipitate was filtered off with suction and washed with methanol. The yield of the dried product, which was virtually pure *trans*-**19**, was 1.045 g (2.66 mmol, 89%). An analytically pure sample of **19** was prepared by sublimation *in vacuo*, mp 346–353° dec.

Anal. Calcd for $C_{26}H_{16}S_2$: C, 79.56; H, 4.11; S, 16.34. Found: C, 79.3; 79.3; H, 4.2, 4.2; S, 16.4, 16.4.

Dinaphtho[1,2-*d*:1′,2′-*d*′]benzo[1,2-*b*:4,3-*b*′]dithiophene (25).—A suspension of 0.50 g of **19** in 0.55 l. of benzene, to which 10 mg of iodine had been added, was irradiated with a Q-700 lamp for 4 hr. A homogeneous yellow-colored solution had been formed, from which the solvent was evaporated. The residue was chromatographed over alumina with benzene. The collected fractions were evaporated to dryness, which left a pale yellow product. The product was recrystallized from benzene; the yield of pure **25** was 0.33 g (66%), mp 294–297°.

Anal. Calcd for $C_{26}H_{14}S_2$: C, 79.96; H, 3.62; S, 16.42. Found: C, 79.8, 80.1; H, 3.6, 3.6; S, 16.4, 16.4.

2-[*β*-(2-Naphtho[2,1-*b*]thienyl)vinyl]benzo[1,2-*b*:4,3-*b*′]dithiophene (20).—In 20 ml of dry methanol were dissolved 0.52 g (2.4 mmol) of the aldehyde **8** and 1.20 g (2.4 mmol) of the phosphonium salt **14** with stirring and slight heating. Through the condenser was added dropwise in 5 min 4 ml of 1.2 *N* $NaOCH_3$ in methanol and the mixture was allowed to reflux for 1 hr. The precipitated product was filtered off with suction, washed with methanol, and dried. The yield of the dry yellow product (almost pure *trans*-**20**) was 0.88 g (2.2 mol, 92%), mp 343–350° dec. An analytically pure sample of *trans*-**20** was obtained by subliming the crude product *in vacuo*.

Anal. Calcd for $C_{24}H_{14}S_3$: C, 72.32; H, 3.55; S, 24.14. Found: C, 72.3, 72.0; H, 3.5, 3.5; S, 24.0, 23.7.

Benzo[*e*]thieno[3,2-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (26).—A suspension of 0.450 g of **20** in 0.55 l. of benzene, to which 10 mg of iodine was added, was irradiated with a Q-700 lamp for 5 hr. A brownish homogeneous solution was obtained from which the product was isolated in the usual way. The yield of the pale yellow **26** was 217 mg (48.5%), mp 216–236° (from benzene).

Anal. Calcd for $C_{24}H_{12}S_3$: C, 72.69; H, 3.05; S, 42.26. Found: C, 72.6, 72.4; H, 3.1; S, 24.3, 24.0.

2,7-Di[*β*-(2-thienyl)vinyl]benzo[1,2-*b*:4,3-*b*′]dithiophene (28).—To 20 ml of dry methanol were added 0.79 g (2.0 mmol) of thenyltriphenylphosphonium chloride[45] and 0.19 g (0.78 mmol) of the dialdehyde **9**. The aldehyde, in contrast with the phosphonium salt, did not dissolve but was actually suspended. The mixture was vigorously stirred and 2.5 ml of 1.7 *N* $NaOCH_3$ in methanol was added. Immediately an orange precipitate was formed. The reaction mixture was allowed to reflux for 0.5 hr and cooled, and the precipitate was filtered off with suction. A crude yield of 272 mg (0.67 mmol, 86%) of product which had mp 230° dec was obtained. A sample was purified by sublimation *in vacuo*.

Anal. Calcd for $C_{22}H_{14}S_4$: C, 65.00; H, 3.47. Found: C, 65.1, 65.1; H, 3.6, 3.6.

Dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (29).—A solution of 50 mg of the compound **28** in 125 ml of benzene, which contained a trace of iodine, was irradiated with a S-81 lamp for 2.5 hr. The resulting solution was worked up according to the general procedure. The product after slow evaporation of a chloroform solution formed yellow needles with mp 268–270°, obtained in a yield of 13 mg (26%).

Anal. Calcd for $C_{22}H_{10}S_4$: C, 65.64; H, 2.51; S, 31.90. Found: C, 65.4, 65.3; H, 2.5, 2.5; S, 31.5, 31.4.

2-Formylbenzo[*e*]thieno[3,2-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (30).—In 50 ml of dry ether 0.50 g (1.26 mmol) of the helicene **26** was dissolved. The solution was stirred magnetically and cooled in an ice–water mixture. The air was expelled from the flask with dry nitrogen and a weak nitrogen flow was maintained during the reaction. With a graduated pipet was added 2 ml of a 2.3 *N* *n*-butyllithium solution in hexane. The cooling bath was removed and the mixture was stirred for 10 min. After that time all of the starting material had dissolved. A solution of 1.0 g (7.4 mmol) of *N*-methylformanilide in 5 ml of ether was added in 5 min and the resulting reaction mixture was stirred for 15 min. The reaction mixture was poured in 50 ml of 1 *N* hydrochloric acid and more ether was added to dissolve the product, which had precipitated partially. The organic layer was washed with water and sodium bicarbonate solution, dried over anhydrous $MgSO_4$, and evaporated to dryness. Some methanol was added to the residue in order to dissolve the readily soluble side products (*e.g.*, *n*-pentanal) and the product was collected by filtration. The crude product (0.43 g) was recrystallized from a mixture of ethanol and benzene. The yield of the pure yellow aldehyde was 0.35 g (0.82 mmol, 65%), with mp 243–245°.[46] Alternatively, the aldehyde could be purified by chromatography over silica gel with chloroform as eluent.

Anal. Calcd for $C_{25}H_{12}OS_3$: C, 70.72; H, 2.84; S, 22.66. Found: C, 70.5, 70.5; H, 3.0, 2.9; S, 22.3, 22.2.

2-[*β*-(2-Naphtho[2,1-*b*]thienyl)vinyl]benzo[*e*]thieno[3,2-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (31).—A solution of 238 mg (0.56 mmol) of the aldehyde **30** and 500 mg (1.0 mmol) of the phosphonium salt **14** in 22 ml of dimethyl sulfoxide was prepared. Approximately 200 mg of sodium hydride (50%) suspension in mineral oil, 4.0 mmol) was added and the mixture was heated on a water bath to 60° with shaking. Subsequently the reaction mixture was poured in 150 ml of water and the aqueous mixture was extracted with three 50-ml portions of ether. The combined ether extracts were washed with water and dried over anhydrous $MgSO_4$. The yellow residue, obtained after evaporation of the ether, was chromatographed over silica gel with benzene as eluent and subsequently over alumina with ether as eluent. The product is eluted as a yellow, but strongly green fluorescent, solution. Evaporation of the solvent yielded 240 mg (0.40 mmol, 71%) of product, mp 194–200° (from benzene–petroleum ether).

Anal. Calcd for $C_{38}H_{20}S_4$: C, 75.42; H, 3.36; S, 21.21. Found: C, 75.4, 75.1; H, 3.6, 3.7; S, 20.3, 20.2.

Bis(naphtho[2,1-*b*]thieno)[1,2-*e*:1′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (32).—A solution of 210 mg of the compound **31** and 2 mg of iodine in 120 ml of benzene was irradiated with a S-81 lamp (under air, 30°) during 12 hr. The green fluorescence of the reaction mixture revealed that some starting material was still present. Evaporation of the solvent and column chromatography of the residue over alumina with benzene eluted a single yellow product which did not fluoresce. The solvent was evaporated until *ca.* 2 ml were left. Addition of pentane completed the precipitation of the undecahelicene. The liquid was removed with a pipet and the precipitate washed with pentane in a similar way. The product was washed with pentane in a similar way. The product was obtained in a yield of 30 mg (14%) and had mp 368–370°.

Anal. Calcd for $C_{38}H_{18}S_4$: C, 75.71; H, 3.01; S, 21.28. Found: C, 75.3, 75.2; H, 3.1, 3.1; S, 20.7, 20.6.

1-(2-Thienyl)-2-(2-benzo[*b*]thienyl)ethene (33).—Benzo[*b*]thiophene-2-carboxaldehyde[23] (1.62 g, 0.01 mol) and diethyl-2-thenylphosphate[20] (2.4 g, 0.01 mol) were dissolved in 20 ml of dry dimethoxyethane in a flask equipped with a reflux condenser. Sodium hydride as a 50% suspension in mineral oil (0.5 g, 0.01 mol) was added and the mixture was refluxed for 0.5 hr. The reaction mixture was cooled and poured in 100 ml of water. The precipitated product was collected by filtration, dried, and recrystallized from ethanol. The pale yellow compound, mp 180–181°, was obtained in 66% yield (1.6 g, 6.6 mmol).

Anal. Calcd for $C_{14}H_{10}S_2$: C, 69.28; H, 4.16; S, 26.46. Found: C, 69.4, 69.2; H, 4.2, 4.2; S, 26.4, 26.2.

[1]Benzothieno[5,4-*b*][1]benzothiophene (34).—A solution of 0.70 g of **33** in 0.55 l. of benzene to which a crystal of iodine had

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(46) The aldehyde proton appears in the nmr spectrum ($CDCl_3$) at unusual high field (τ 1.03) as a result of the deshielding effect of the underlying benzene ring.

been added was irradiated with a Q-700 lamp for 2.5 hr. The product was isolated in the usual manner. The yield of the colorless compound was 0.51 g (73%), mp 149–150°, after recrystallization from a benzene–petroleum ether (bp 40–60°) mixture.

Anal. Calcd for $C_{14}H_8S_2$: C, 69.97; H, 3.35; S, 26.69. Found: C, 70.1, 70.3; H, 3.3, 3.2; S, 26.7, 26.5.

Reaction of the Hexaheterohelicenes with Aluminum Chloride.—To a solution of 100 mg of the hexaheterohelicene **22** or **24** in 15 ml of benzene was added 200 mg of anhydrous aluminum chloride. After standing for 24 hr the reaction mixture was p3ured in water. The benzene layer was separated, dried over anhydrous K_2CO_3, and evaporated. The residue was chromatographed *over alumina with benzene. Evaporation of the* benzene left a single product in each case. The compound **24** afforded 10 mg (10%) of the pale yellow highly insoluble compound **38**, mp 359–363°, whereas **22** gave 17 mg (17%) of the yellow compound **37**, mp 267–280°. The nmr spectra of the compounds were complex; most characteristic was the absence of shielded protons. The mass spectrum (70 eV) of **22** showed only strong peaks at *m/e* 338 (M^+) and 169 (M^{2+}); mass spectrum (70 eV) of **24**, *m/e* (rel intensity) 344 (M^+, 100), 310 (2.8), 299 (9.5), 232 (6.3), 172 (M^{2+}, 37).

Resolution and Attempted Resolution of 21–26 by Crystal Picking.—In 10 ml of benzene (p.a.) in a 100-ml beaker was dissolved 10–50 mg of the helicene. The beaker was covered with a piece of filter paper and then with a glass plate. After standing for 1–3 days the solvent had completely evaporated leaving large and pure pale yellow crystals. Sometimes the crystals were well separated and could easily be picked, but in other cases they were grown together and difficult to separate. The compounds **22** and **26** could easily be resolved by selecting well-shaped crystals, dissolving them separately in chloroform, and measuring the optical rotation. The hexahelicene **24** gave more difficulties. After the first crystallization from benzene only one of the fourteen picked crystals showed optical activity. Better results were obtained by using toluene rather than benzene. The dissymmetric heptahelicenes **25** and **29** withstood all attempts to resolve it by simple crystallization techniques.

The measurements were carried out with solutions of single crystals in 1.0 ml of $CHCl_3$ (p.a.) in a 5-cm cell, mostly at 436 mμ which is the strongest emission line of the Zeiss polarimeter used. The temperature was approximately 25°. The results of some of the measurements are collected in the Tables III and IV. The measured rotations are accurate to 0.005°; the error in the specific rotations is approximately 5%.

TABLE III

OPTICAL ROTATION OF SOME CRYSTALS AT 436 mμ

Compd	Wt of crystal, mg	Measured rotation, α, deg	Specific rotation, $[\alpha]$, deg
22	0.59	+0.170	+580
	0.47	+0.060	+260
	0.53	−0.515	−1950
	0.35	−0.385	−2200
	0.40	−0.190	−950
	0.22	+0.480	+4360
	0.016[a]	−0.045	−5600
24	0.22	+0.400	+3640
	0.89	+1.30	+2920
	0.14	−0.245	−3500
26	0.89	+0.240	+540
	0.58	+0.090	+310
	0.51	−0.050	−200
	0.16	+0.420	+5240
	0.44	−0.050	−220
	0.068[a]	+0.245	+7200

[a] Single crystals.

TABLE IV

VARIATION OF THE LONG WAVELENGTH OPTICAL ROTATION (ZEISS POLARIMETER)

	Highest measured specific rotation (25°, $CHCl_3$)			
Compd	405 mμ	436 mμ	546 mμ	578 mμ
26	+9000°	+7200°	+3000°	+2500°
22	−5700°	−5600°	−2600°	−2300°
24	+2360°	+3640°	+1800°	+1460°

Resolution of 26 by Recrystallization from (−)-α-Pinene.—The heptahelicene **26** was divided in 50-mg quantities and these were dissolved in 10 ml of (−)-α-pinene with heating. The solutions were allowed to cool either at room temperature or in a refrigerator at −25°. The crystallized material was separated from the solution by decantation, thoroughly washed with petroleum ether (bp 60–80°) to remove the solvent, and dried. The total amount of crystals (actually a pale yellow powder) was dissolved in 1.0 ml of chloroform and the optical rotation measured in a 5-cm cell. The results are shown in Table V.

TABLE V

Recovered material, mg	Conditions of crystallization	Measured rotation, α^{25}_{436}, deg	Specific rotation, $[\alpha]^{25}_{436}$, deg
7	−25° (4 days)	+3.60	+1000
13	−25° (1 day)	+2.43	+370
4	−25° (4 hr)	+4.27	+2400
16	+20° (1 day)	+0.27	+34

In the first two runs petroleum ether was added to the mother liquor. The precipitated helicene was collected and washed as before, which afforded 10 and 6 mg, respectively. These fractions showed a negative optical rotation, α^{25}_{436} = −2.65 and −0.82°, respectively, corresponding with specific rotations of −530 and −270°. Recrystallization of **26** under similar conditions from a toluene–petroleum ether mixture (50:50) resulted in a 70% recovery of completely inactive material. Recrystallization from methylcyclohexane (15 ml/50 mg) resulted in beautiful crystals each of which was active. The total amount of crystals (50% of the dissolved amount) showed no optical rotation, however. Attempts to resolve the heptahelicene **25** with the previous method was unsuccessful; the crystallizate showed no significant optical rotation.

Synthesis of Partially Resolved 32.—Partially resolved heptahelicene **26** was used for the synthesis of an optically active sample of the undecahelicene **32**. The starting material weighed 15 mg and showed the following specific optical rotations (in $CHCl_3$): $[\alpha]^{25}_{436}$ = +220°; $[\alpha]^{25}_{578}$ = +188°. Comparison with the highest measured values shows that the optical purity cannot be more than 7.6%. The helicene was converted to the aldehyde **30** described earlier for the racemate with the modifications that slightly more solvent was used (4 ml of ether) and that the product was not recrystallized but purified by chromatography over silica gel with benzene. The optical rotation of the aldehyde was not measured accurately but it was also positive and not much different from the starting material. The aldehyde was converted to the alkene, as described for the racemate. The specific optical rotation of this compound was found to be $[\alpha]^{25}_{578}$ = +140°. Irradiation of the alkene (*ca.* 8 mg) in 120 ml of benzene with a S-81 lamp for 3 hr with a trace of iodine and work-up as usual gave 1.12 mg (determined with uv spectroscopy) of optically active **42**. The specific rotation ($CHCl_3$) of the product was $[\alpha]^{25}_{546}$ = +270°, $[\alpha]^{25}_{578}$ = +214°. Taking into account the optical purity of the compound (less than 7.6%), the specific rotations of the optically pure **32** have to be at least +2600° at 546 mμ and +2000° at 578 mμ.

Lithiation and Deuteration of 4, 24, and 26.—To a solution of 100 mg of compound **4**, **24** and **26** in 15 ml of dry ether was added under nitrogen an excess of *n*-butyllithium (*ca.* 1 ml, 2.3 *N*) in hexane. The mixture, kept under nitrogen, was allowed to reflux for 0.5 hr. After addition of 1 ml of deuterium oxide the reaction mixture was stirred for 10 min. The reaction mixture was washed with water and dried (anhydrous $MgSO_4$). After evaporation of the ether almost quantitative yields of crude dideuterio-**4** and monodeuterio-**24** and -**26** were obtained. In all cases the starting material showed in the nmr spectrum two doublets (J = 5.5 cps) due to the thiophene protons. One of these doublets (assigned to the α protons) disappeared on deuteration, whereas the other (assigned to the β protons) collapsed to a singlet.

Registry No.—**7**, 18703-68-9; **8**, 30689-46-4; **9**, 30689-47-5; **11**, 30689-48-6; **12**, 30689-49-7; **13**, 30689-50-0; **14**, 30439-20-4; *cis*-**15**, 30689-52-2; *trans*-**15**, 30689-53-3; *cis*-**16**, 30689-54-4; *trans*-**16**, 30689-55-5; **17**, 30689-56-6; *trans*-**18**, 30689-57-7; *trans*-**19**, 30689-58-8; **20**, 30689-59-9; **22**, 20841-66-1; **23**, 30689-61-3; **24**, 24132-27-2; **25**, 30689-63-5; (+)-**26**, 30412-89-6; **28**, 30689-65-7; **29**, 30689-66-8; **30**, 30758-78-2; **31**, 30758-79-3; (+)-**32**, 30412-92-1; **33**, 30689-68-0; **34**, 30758-80-6; **37**, 30689-69-1; **38**, 30689-70-4.

Nucleosides. XIII. The Concurrent Introduction of Two Different Blocking Groups Into Some Ribonucleosides[1a,b]

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The reaction of adenosine, cytidine, and guanosine with *p*-nitrobenzaldehyde and ethyl orthoformate in the presence of trifluoroacetic acid in dimethylformamide affords the corresponding *N*-(α-ethoxy-*p*-nitrobenzyl)-2′,3′-*O*-ethoxymethylene derivatives **1a**, **3b**, and **4**, respectively, in excellent yields. Benzoylation of **1a** in pyridine effected, as well, concurrent elimination of the elements of ethanol to give the 5′-*O*-benzoyl-*N*-(*p*-nitro)benzylidene derivative **2**. On the other hand, uridine and *p*-nitrobenzaldehyde in the presence of *p*-toluenesulfonic acid gave 2′,3′-*O*-*p*-nitrobenzylideneuridine (**5a**). Possible reaction paths for these transformations, which constitute useful procedures for the simultaneous introduction of two different blocking groups into certain nucleosides, are discussed.

Several useful procedures have been developed for masking the cis glycol system of a ribonucleoside by condensation with a suitable aldehyde or ketone under acid catalysis. Unfavorable equilibria that arise in certain cases of acetal and ketal formation can be overcome through the use of ketals[2] or ethyl orthoformate.[3,4] The latter has also found application in effecting acetal formation with benzaldehyde and derivatives thereof that carry a para substituent capable of increasing electron density at the carbonyl function by resonance (R^+) effects.[5] By contrast, 2′,3′-*O*-benzylidene nucleosides that carry a para (R^-) substituent are, to our knowledge, unknown. The present communication describes the results of an attempt to prepare 2′,3′-*O*-(*p*-nitrobenzylidene)adenosine, which was required in an unrelated study, and which led instead to a novel and useful procedure for the concurrent introduction of two different blocking groups into certain nucleosides.

The reaction of adenosine and excess *p*-nitrobenzaldehyde in a mixture of dimethylformamide (DMF) and ethyl orthoformate containing trifluoroacetic acid gave a chromatographically homogeneous solid (90% yield) to which the structure N^6-(α-ethoxy-*p*-nitrobenzyl)-2′,3′-*O*-ethoxymethyleneadenosine (**1a**) was assigned on the basis of chemical and spectral (ir, uv, and nmr) evidence along with both elemental and ethoxyl analyses. The absence of a free amino group in the structure, which was evident from its ir spectrum ($CHCl_3$), was confirmed by the failure of **1a** to react with dimethylformamide dimethyl acetal.[6] The hydrolysis of **1a** with 88% formic acid at room temperature for 5 min gave *p*-nitrobenzaldehyde and adenosine 2′(3′)-formate. The latter was shown to be identical with the product of formic acid hydrolysis[7] of 2′,3′-*O*-ethoxymethyleneadenosine (**1b**).[8]

The benzoylation of **1a** in pyridine at room temperature promoted the elimination of the elements of ethanol from the N,O mixed acetal in addition to effecting esterification of the primary (C′-5) alcohol residue and thereby provided the Schiff base **2**.

Cytidine, like adenosine, gave the corresponding N,O mixed acetal **3b** in high yield. Surprisingly, the yield of the corresponding derivative of cytosine **3a** is significantly lower (35%) under the same conditions with 55% of the heterocycle being recovered unchanged. Acid hydrolysis of **3a** and **3b** afforded *p*-nitrobenzaldehyde and cytosine [or cytidine-2′(3′)-formate]. The latter was easily hydrolyzed in alkali to cytidine.

The same reaction applied to guanosine gave a (tlc) chromatographically homogeneous solid which, on acid hydrolysis, yielded *p*-nitrobenzaldehyde and guanosine 2′(3′)-formate as the only detectable products. Accordingly, the structure N^4-(α-ethoxy-*p*-nitrobenzyl)-2′,3′-*O*-ethoxymethyleneguanosine (**4**) was assigned to the product. Whereas this assignment is supported by spectral (ir, uv) data, all attempts to obtain an acceptable elemental analysis have been unsuccessful.

The importance of ethyl orthoformate to the formation of the mixed acetals is indicated by the fact that adenosine is recovered unchanged when the ortho ester is omitted from the reaction mixture. These observa-

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