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THE SYNTHESIS AND SPECTRA OF SOME HETEROCYCLIC FULVALENES

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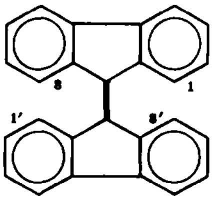
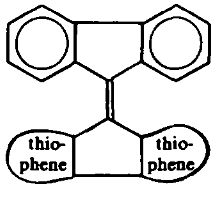
Abstract—The heterofulvalenes X-XIV, XXIII and XXVI have been synthesized. The effect of overcrowding on their spectral properties is discussed. The last step in the synthetic schemes is a dehydration reaction of the appropriate carbinols. The great difference in reactivity of these intermediate carbinols in the dehydration reactions is striking.

INTRODUCTION

THE chemistry of $\Delta^{9,9'}$-bifluorene (I) has been the subject of many investigations in the widest sense.[1] Especially the problem of the detailed spatial structure of I has been studied theoretically and experimentally. The steric interaction of the H atoms in the positions 1,1',8 and 8' makes a planar structure of the molecule impossible. Recent work by Bailey and Hull[2] shows that in the solid state some substituted $\Delta^{9,9'}$-bifluorenes have a twisted conformation (indicating a partial radical character of the central double bond) rather than the folded conformation as reported for unsubstituted $\Delta^{9,9'}$-bifluorene (I) by earlier workers.[3,4] The inadequacy of the very limited data used in the earlier investigation and initial work by Bailey and Hull throws doubt on the accuracy of the reported structure of I. From the absorption spectrum of I it has been concluded that in solution the molecule has a partial diradical character.[5] By means of an LCAO–MO calculation Stegemeyer[6] could explain the experimental results assuming a twist of 40° around the central double bond. In the NMR spectrum of I there appears a distinct absorption at low field due to the four H atoms that crowd the central double bond. Bergmann *et al.*[7] submit that this absorption at low field reflects an interaction between these four H atoms. It seemed worthwhile to synthesize some heterocyclic overcrowded fulvalenes of types II and III, to study the spectral properties in a number of closely related systems. Comparing these heterocyclic fulvalenes there should be a difference in steric requirements as well as in the electronic properties due to the annellation of the thiophene rings.



I



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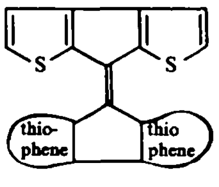

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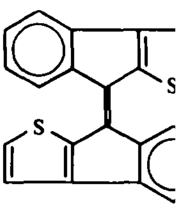
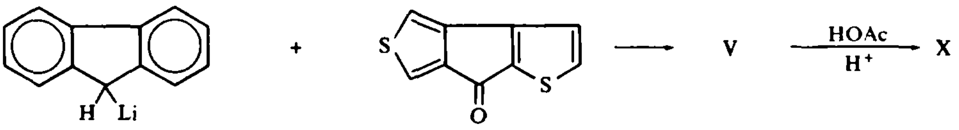


IV

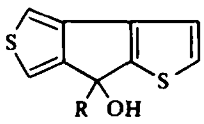
Brule and Le Bihan[8] recently prepared some heterocyclic fulvalenes with indenothiophene moieties (e.q. IV) from the reaction of 8*H*-indeno[2,1-*b*]thiophene-8-one and $W(CO)_6$. From the NMR spectrum they concluded that fulvalene IV had the *trans*-configuration.

Synthesis

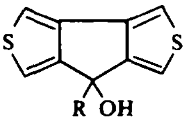
Although many different routes[1,5] have been described to synthesize $\Delta^{9,9'}$-bifluorene all these reactions failed in the cyclopentadithiophene series and only the route as described for heterofulvalene X succeeded in our case:



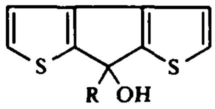
From 9-fluorenyllithium and the appropriate cyclopentadithiophenones[9] the carbinols V-IX could be prepared in reasonable yields (Table 1). The elementary analysis, NMR and IR spectra (Table 1) of these carbinols are in accord with the structures assigned. The compounds are very sensitive to traces of base and acid and elevated temperatures. In the case of base treatment a retro-reaction takes place to yield fluorene and the appropriate cyclopentadithiophenone, while under the influence of acid or heat unidentified materials were formed. The position of the O-H protons in the NMR spectra were determined by D_2O exchange experiments.



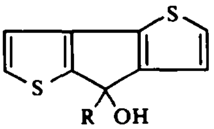
V



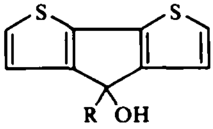
VI



VII



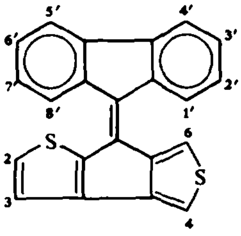
VIII



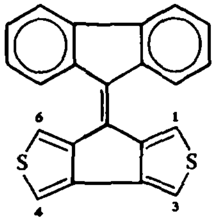
IX

R — 9-fluorenyl

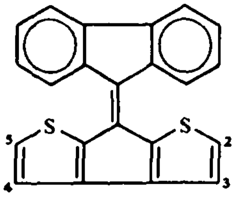
The dehydration of the fluorenylhydroxycyclopentadithiophenes could be achieved in acetic acid with 1-3 drops concentrated hydrochloric acid. All other dehydration methods like oxalylchloride, P_2O_5, thionylchloride in pyridine, *p*-toluenesulfonic acid in benzene, HBr gas in acetic acid, PBr_2 in benzene and BF_3 in ether failed to yield fulvalenes.



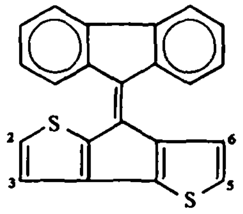
X



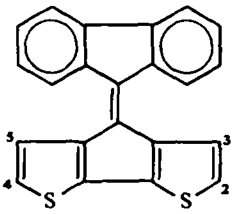
XI



XII

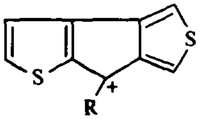


XIII

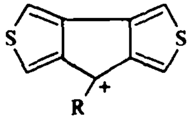


XIV

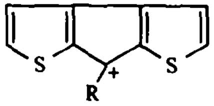
The great difference in reactivity of the intermediate carbinols in the dehydration reactions is particularly interesting. The carbinols V and VI are dehydrated to the fulvalenes X and XI at room temperature in high yields (~ 90%). Carbinol VII is dehydrated at some higher temperature (60°) and affords the fulvalene XII in 41% yield. On the other hand the carbinols VIII and IX can be dehydrated in acetic acid with hydrochloric acid at the boiling point (118°), so that it is not surprising that the yields of the fulvalenes XIII and XIV are poor (respectively 24 and 7%), since under these reaction conditions decomposition of the carbinols as well as that of the formed fulvalenes occurs. The prediction that the more stable the intermediate cation the easier the dehydration reaction occurs was supported by calculations of the difference in stability of the six cyclopentadithiophene cations.[10] From these calculations it turns out that *in the following series there is a decrease in stability of the cations from* XV to XIX.



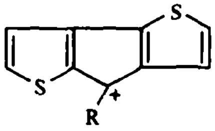
XV



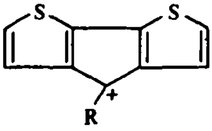
XVI



XVII



XVIII



R — 9-fluorenyl

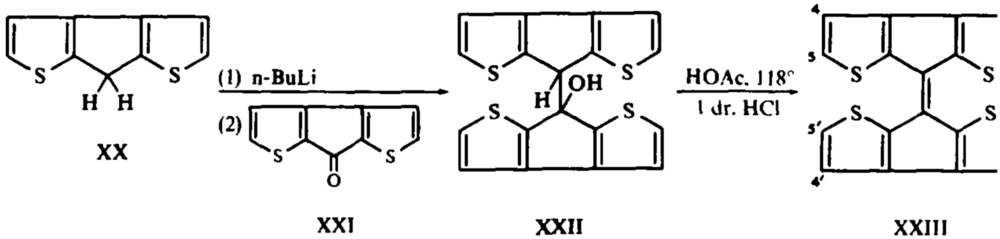
XIX

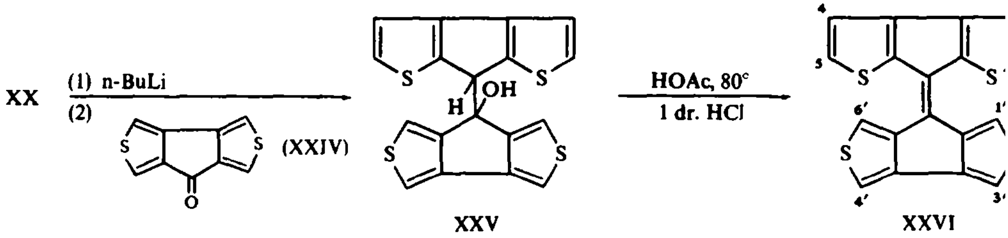
TABLE 1. FLUORENYLHYDROXYCYCLOPENTADITHIOPHENES

	Compound	Yield	m.p.	IR (KBr)		NMR spectra in CD_3COCD_3 (δ in ppm)				Analysis	
			(dec.)	ν_{OH} in cm^{-1}	OH	Methylene proton	Thiophene protons		Benzene protons	Calc.	Found
VII	7-Hydroxy-(7,9′-fluorenyl)-7*H*-Cyclopenta-[1,2-b:4,3-b′]dithiophene	68%	160–192°	3505	5·49 (s, 1H)	4·70 (s, 1H)	6·87 (d, 2H) 7·25 (d, 2H)	J = 5·0 cps	7·00–7·42 (m, 6H) 7·69 (m, 2H)	C, 73·71 H, 3·93 S, 17·89	73·91 3·79 17·79
VIII	7-Hydroxy-(7,9′-fluorenyl)-7*H*-Cyclopenta-[1,2-b:3,4-b′]dithiophene	74%	178–180°	3250	5·31 (s, 1H)	4·76 (s, 1H)	6·82 (d, 1H) 6·98 (d, 1H) 7·08 (d, 1H) 7·28 (d, 1H)	J = 5·2 cps J = 5·0 cps	6·90–7·40 (m, 5H) 7·50–7·80 (m, 3H)	C, 73·71 H, 3·93 S, 17·89	74·01 3·98 17·56
IX	4-Hydroxy-(4,9′-fluorenyl-4*H*-Cyclopenta-[2,1-b:3,4-b′]dithiophene	85%	158–160°	3250	5·15 (s, 1H)	4·77 (s, 1H)	6·52 (d, 2H) 7·06 (d, 2H)	J = 5·1 cps	7·15–7·37 (m, 6H) 7·59–7·75 (m, 2H)	C, 73·71 H, 3·93 S, 17·89	73·92 4·03 17·35
V	7-Hydroxy-(7,9′-fluorenyl)-7*H*-Cyclopenta-[1,2-b:3,4-c′]dithiophene	52%	150–201°	3495	5·38 (s, 1H)	4·76 (s, 1H)	6·88 (d, 1H) 6·91 (d, 1H) 6·90 (d, 1H) 7·19 (d, 1H)	J = 2·0 cps J = 5·0 cps	7·00–7·73 (m, 8H)	C, 73·71 H, 3·93 S, 17·89	73·75 3·87 17·95
VI	7-Hydroxy-(7,9′-fluorenyl)-7*H*-Cyclopenta-[1,2-c:3,4-c′]dithiophene	71%	135–180°	3270	5·22 (s, 1H)	4·75 (s, 1H)	6·68 (d, 2H) 7·04 (d, 2H)	J = 2·2 cps	7·11–7·43 (m, 6H) 7·57–7·75 (m, 2H)	C, 73·71 H, 3·93 S, 17·89	74·09 4·05 17·25

Cations XVII, XVIII and XIX formally analogous to the cyclopentadiene cation, have anti-aromatic character, thus their instability is not surprising. It is then not astonishing that the dehydration of carbinol V to fulvalene X, in which cation XV is the intermediate, can occur under gentle conditions while on the other hand in these series fulvalene XIV is formed only under the most forced conditions because cation XIV is not easily generated.

The successful synthesis of heterofulvalenes of type II was applied also to the preparation of two isomers of type III. The lithiation of 7*H*-cyclopenta[1,2-*b*:4,3-*b*′]-dithiophene[11] (XX) with n-butyllithium in ether occurred on the methylene bridge which appeared from the reaction with 7*H*-cyclopenta[1,2-*b*:4,3-*b*′]dithiophene-7-one[9] (XXI) and 7*H*-cyclopenta[1,2-*c*:3,4-*c*′]dithiophene-7-one[9] (XXIV) to the carbinols XXII and XXV respectively.





The NMR spectrum of XXII shows in addition to the aromatic absorptions, singlets for the OH-absorption and methylene proton at $\delta = 4{\cdot}00$ and $\delta = 4{\cdot}70$ respectively. Compound XXV showed these values at $\delta = 5{\cdot}39$ (OH) and $\delta = 4{\cdot}76$ (methylene H). In the IR spectra (KBr) of XXII and XXV the OH absorptions are present at 3500 cm^{-1} and 3307 cm^{-1} respectively.

Carbinols XXII and XXV could be dehydrated in acetic acid with hydrochloric acid to the heterofulvalenes XXIII and XXVI in 66% and 76% respectively. The spectral properties (Tables 2 and 3) and elemental analyses are in complete agreement with the structures assigned.

The spectra

In the IR spectrum of $\Delta^{9,9'}$-bifluorene (I) are three characteristic vibrations[12,13]: (a) a very weak band at 1605 cm^{-1} due to the aromatic rings; (b) an absorption at 1362 cm^{-1} which is characteristic of the 5-membered ring; (c) The out of plane C—H deformation vibrations at 720 and 770 cm^{-1}. These last mentioned vibrations

TABLE 2. NMR SPECTRA OF THE HETEROFULVALENES (δ IN PPM)

	Solvent	H-1′ and H-8′	H-4′ and H-5′	H-2′ and H-3′ H-6′ and H-7′	H-1	H-2	H-3	H-4	H-5	H-6	Coupling constants (cps)
X	CCl_4	8·59 (m)	7·62 (m)	7·23 (m)		7·25 (d)	7·01 (d)	6·81 (d)		7·82 (d)	$J_{23} = 5·2$ $J_{46} = 2·0$
XI	$CDCl_3$	8·61 (m)	7·76 (m)	7·32 (m)	7·98 (d)		7·15 (d)	7·15 (d)		7·98 (d)	$J_{13} = 2·3$
XII	$CDCl_3$	8·88 (m)	7·63 (m)	7·33 (m)		7·30 (d)	6·96 (d)	6·96 (d)	7·30 (d)		$J_{23} = 5·0$
XIII	CCl_4	8·68 (m)	7·53 (m)	7·18 (m)		7·53 (d)	6·93 (d)		7·25 (d)	6·97 (d)	$J_{23} = 5·0$
XIV	$CDCl_3$	8·25 (m)	7·58 (m)	7·25 (m)		7·00 (d)	6·52 (d)	7·00 (d)	6·52 (d)		$J_{56} = 5·0$
		H-2 (H-5, H-2′, H-5′)		H-3 (H-4, H-3′, H-4′)							
XXIII	$CDCl_3$	7·46 (d)		7·14 (d)							$J_{23} = 5·0$
		H-1′ (H-6′)		H-3′ (H-4′)		H-2 (H-5)		H-3 (H-4)			
XXVI	CD_3SOCD_3	8·49 (d)		7·72 (d)		7·78 (d)		7·30 (d)			$J_{1'3'} = 2·0$ $J_{23} = 5·0$

are strongly affected by the central double bond which also explains the two absorptions in the 700–800 region instead of one band like fluorene. The IR spectra of the heterofulvalenes closely resemble those of $\Delta^{9,9'}$ -bifluorene (I). Only compound XXIII which lacks the ortho-H atoms, shows no strong bond in the 770 cm^{-1} region and no weak absorption at about 1600 cm^{-1} (Experimental).

From the NMR spectrum of I it turned out that the absorption of four protons at low field ($\delta = 8{\cdot}31$ in $CDCl_3$) reflects an interaction between the ortho-protons in the 1,1′,8 and 8′ positions.[7] The NMR spectra of the heterofulvalenes are recorded in Table 2. It appears that the H atoms of the fulvalenes X-XIV in the position 1′ and 8′ of the fluorene moiety give a resonance at still lower field (with the exception of XIV) than in I. For a planar molecule[6] of I the distance between the non-bonding atoms in the ortho positions are $r_{HH} = 0{\cdot}7$ and $r_{CC} = 2{\cdot}5$Å. Because the first value is far under the double of the Van der Waals-radius of hydrogen (2·4Å) and distances $r_{CC} < 2{\cdot}9$Å do not appear, a planar conformation of I is unlikely. Bergmann *et al.*[7] have concluded from the NMR spectrum of I that the twist in the $\Delta^{9,9'}$-bifluorene molecule must be limited to a degree which still permits interaction between the ortho-H atoms. For planar molecules of the heterofulvalenes X-XIV, XXIII and XXVI the distances between the atoms in the ortho positions are about $r_{HH} = 1{\cdot}2$Å (X, XI, XIII, XIV), $r_{CC} = 2{\cdot}8$Å (X, XI, XIII, XIV), $r_{HS} = 1{\cdot}9$Å (X, XII, XIII), $r_{CS} = 2{\cdot}9$Å (X, XII, XIII), $r_{SS} = 2{\cdot}9$Å (XXIII), $r_{HS} = 2{\cdot}1$Å (XXVI) and $r_{CS} = 3{\cdot}0$Å (XXVI).

The Van der Waals radius of carbon is 1·6Å and of sulphur 1·85Å. Although the steric hinder in all of these heterofulvalenes is less than in I, planar conformations are still unlikely. The overcrowding in the heterofulvalenes X-XIV finds expression in the absorptions at low field (Table 2) due to the H atoms in the 1′ and 8′ positions and is caused by the deshielding effect by thiophene rings. This deshielding seems to be stronger than the deshielding of the benzene rings in I on the protons 1,1′,8 and 8′. However the shift to very low field might also—in part—be of electronic nature. From Table 2 it is clear that for compounds X and XI the "ortho"-thiophene protons are deshielded by the benzene rings ($\delta = 7{\cdot}82$ and $7{\cdot}98$ respectively) but in XIII and XIV it is strange that the "ortho"-protons, which are β-thiophene protons do not absorb at low field. On comparing the fulvalenes XI and XXIII it is noteworthy that in XXIII not only the "ortho"-thiophene protons absorb at much lower field than in XI ($\delta = 8{\cdot}49$ and $7{\cdot}98$ respectively) but also the remaining thiophene protons. It is reasonable to conclude that electronic effects play an important role in this case. These shifts to lower field of "non ortho"-thiophene protons is less striking when comparing XII and XXIII.

The UV absorption maxima of the heterofulvalenes and $\Delta^{9,9}$-bifluorene (I) are recorded in Table 3. The resemblance between the absorption spectra of all of the heterofulvalenes and I is very great. The spectrum of XXIII shows much vibrational structure. The loss of fine structure in annelating aromatic compounds has been attributed to the overcrowding in the molecules although this effect was not observed in overcrowded helicenes.[3,14,15] From a steric view-point it is clear that the overcrowding in XXIII is less than in the other heterofulvalenes, so that it is possible that XXIII is more planar, resulting in more fine structure in its absorption spectrum. The long wave length band, at 458 nm, in $\Delta^{9,9}$-bifluorene (I) has been attributed to a twist of about 40° of the aromatic systems around the central double bond.

It seems reasonable to assume a similar twist in the heterofulvalenes X-XIV because of the great similarity of the absorption spectra of I and the compounds X-XIV. The exact amount of twist cannot be stated at present.

TABLE 3. UV SPECTRA OF THE HETEROFULVALENES AND $\Delta^{9,9'}$-BIFLUORENE IN CYCLOHEXANE λ_{max}, Mμ (LOG ε)

Compound	
I	244 (4·90), sh 264 (4·58), 273 (4·64), 280 (4·57), 340 (3·30), 460 (4·38)
X	sh 245 (4·69), 251 (4·72), 270 (4·53), 320 (3·41), 345 (3·48), 360 (3·50), 450 (4·23)
XI	250 (4·82), 265 (4·67), sh 278 (4·55), 330 (3·68), 436 (4·32)
XII	sh 237 (4·56), 242 (4·62), sh 252 (4·53), 272 (4·53), 280 (4·52), 345 (3·72), 454 (4·33)
XIII	sh 234 (4·52), 242 (4·62), 270 (4·59), 277 (4·55), 343 (3·64), 440 (4·39)
XIV	sh 237 (4·64), 242 (4·70), 270 (4·67), 277 (4·63), 340 (3·73), 440 (4·48)
XXIII	213 (4·51), 246 (4·33), 272 (4·27), sh 318 (3·47), 330 (3·71), 345 (4·00), 363 (4·13), sh 395 (3·98), 414 (4·35), 440 (4·50)
XXVI	213 (4·57), sh 254 (4·57), 262 (4·60), 279 (4·45), 316 (3·73), 329 (3·86), 345 (3·85), sh 398 (4·22), 419 (4·33)

EXPERIMENTAL

NMR spectra were obtained using a Varian A-60 spectrometer with TMS ($\delta = 0$) as an internal standard. UV spectra were recorded in cyclohexane on a Zeiss PMQ II spectrophotometer. IR spectra were determined in KBr plates on a Perkin Elmer "Grating Spectrophotometer" (model 125). All mp's are uncorrected. The microanalyses were carried out in the Analytical Section of our Department under the direction of Mr. W. M. Hazenberg. The NMR data are presented as chemical shifts in ppm, expressed on the delta-scale ($\delta_{TMS} = 0$) followed by, respectively, a designation of the multiplicity of the signal (s = singlet, d = doublet, m = multiplet), the relative area of the signal, the coupling constants involved, and the assignment of the signal.

The yields, mp's, IR spectra and NMR spectra of the fluorenylhydroxycyclopentadithiophenes are recorded in the Table 1. The NMR and UV spectra of the heterofulvalenes are recorded in the Tables 2 and 3.

Standard method for the preparation of fluorenylhydroxycyclopentadithiophenes V-IX To a soln of 2·2 ml 1·44 N n-BuLi in ether was added in an atmosphere of N_2 a soln of 462 mg (2·75 mmole) of fluorene in 15 ml abs ether which coloured the soln yellow. After adding, the mixture was refluxed for another 45 min. To the cooled mixture 450 mg (2·34 mmole) of the appropriate cyclopentadithiophenone[9] soluted in 25 ml abs ether was added dropwise, after which the mixture was stirred at room temp for 2 hr. The Li salt was decomposed by adding a 10% $NaHCO_3$ aq. The ether layer was separated and washed with water. After drying over $NaSO_4$ and removal of the ether, the residue was dissolved in a little warm CCl_4 (40–60°) and then cooled. After suction on a Büchner funnel the impure product was crystallized from CCl_4 and recrystallized from a benzene-hexane. This last crystallization is necessary because the carbinols which are crystallized only from CCl_4 contain one molecule of this solvent. The properties of the different carbinols are recorded in Table 1.

7-(9'-Fluorenylidene)-cyclopenta[1,2-b:3,4-c']*dithiophene* (*X*). 90 mg (0·25 mmole) of V was dissolved in 10 ml AcOH after which 1 drop conc HCl was added. The yellow soln was stirred for 10 min and then worked up as for XII. Fulvalene X crystallized from hexane as orange needles, m.p. 155–156°, yield 80 mg (93%); IR 1608 (w), 1320 (w), 1345 (m), 710 (s), 730 (s), 771 (s), 790 (s) cm^{-1}. (Found: C, 77·54; H, 3·53; S, 18·76. $C_{22}H_{12}S_2$ requires C, 77·61; H, 3·56; S, 18·83%).

7-(9'-Fluorenylidene)-cyclopenta[1,2-c:3,4-c']*dithiophene* (XI). To a soln of VI (105 mg; 0·29 mmole) in 10 ml AcOH at 35° was added 1 drop of conc HCl. The yellow soln was cooled down to 25° in 1 hr. The work up was the same as for fulvalene XII but the chromatography was carried out with hexane-ether 100:1 as the eluent. The yield after crystallization from petrol (60–80°) was 88 mg (88%), m.p. 182–183°, IR 1602 (w), 1350 (w), 719 (s), 726 (s), 774 (s), 788 (s), 796 (s) cm^{-1}. (Found: C, 77·71; H, 3·71; S, 18·77. $C_{22}H_{12}S_2$ requires: C, 77·61; H, 3·56; S, 18·83%).

7-(9'-Fluorenylidene)-cyclopenta[1,2-b:4,3-b']*dithiophene* (XII). 125 mg (0·35 mmole) of VII was dissolved in 10 ml of AcOH at 35°, after which 3 drops of conc HCl were added. The mixture was heated for 1 hr at 60° which resulted in a very dark red brown soln. After cooling the mixture was poured into water and extracted with ether. After drying over Na_2SO_4 and removal of the solvent, the residue was chromatographed over a silica gel column using hexane. After evaporation of the soln a dark purple product was obtained. One crystallization from petrol (60°–80°) furnished 48 mg (41%) of XII, m.p. 173–174°; IR 1605 (w), 1350 (m), 713 (s), 728 (s), 777 (s) cm^{-1}. (Found: C, 77·57; H, 3·54; S, 18·83. $C_{22}H_{12}S_2$ requires: C, 77·61; H, 3·56; S, 18·83%).

7-(9′-*Fluorenylidene*)-*cyclopenta*[1,2-b:3,4-b′]*dithiophene* (XIII). To a soln of VIII (150 mg; 0·42 mmole) in 20 ml boiling AcOH two drops of conc HCl were added which coloured the soln orange brown. After boiling for 5 min the mixture was cooled and worked up as described for XII except that the chromatography was carried out with hexane-CCl_4 2:1 as the eluent. One crystallization from petrol (60–80°) afforded 35 mg (24%) of purple brown needles m.p. 144–145°; IR 1606 (w), 1348 (m), 715 (s), 723 (s), 772 (s) cm^{-1}. (Found: C, 77·31; H, 3·55; S, 18·71. $C_{22}H_{12}S_2$ requires: C, 77·61; H, 3·56; S, 18·83%).

4-(9′-*Fluorenylidene*)-*cyclopenta*[2,1-b:3,4-b′]*dithiophene* (XIV). To a soln of IX (205 mg; 0·57 mmole) in 20 ml boiling AcOH, two drops of conc HCl were added, causing an immediate yellow colour. The mixture was refluxed for another 30 min after which the colour of the soln was orange brown. The work up was carried out as for XII except that in the chromatography CCl_4 was used. After one crystallization from hexane 14 mg (7%) of very dark green needles were obtained, m.p. 171–173°; IR 1605 (w), 1321, 1350, 1369 (m), 739 (s), 782 (m) cm^{-1}. No elemental analysis was obtained from this fulvalene, but the spectral data, including its mass spectrum ($m/e = 340$) are in complete agreement with the proposed structure.

7,7′-*Bi*-7H-*cyclopenta*[1,2-b:4,3-b′]*dithiophene-7-ol* (XXII). To a soln of 1·60 ml 1·44N n-BuLi in ether at room temp under an atm of N_2 was added dropwise 356 mg (2·0 mmole) 7*H*-cyclopenta[1,2-*b*:4,3-*b′*]-dithiophene[11] in 20 ml ether. After addition was complete the mixture was stirred for 15 min at room temp and then refluxed for another 30 min. To the cooled mixture was added a soln of 364 mg (1·90 mmole) 7*H*-cyclopenta[1,2-b:4,3–*b′*]dithiophene-7-one[9] in 20 ml ether. The green colour which had formed disappeared and a ppt appeared. After stirring for 2 hr a 10% NH_4Cl soln was added. The ether layer was separated and the aqueous phase extracted with a mixture of THF-ether 2:1. The combined ethereal extracts were dried over $MgSO_4$ and after removal of the solvents a dark brown solid remained. This was washed with benzene and pressed in a Büchner funnel. Crystallization from EtOAc afforded 535 mg (76%) white crystals, m.p. 250° (dec); NMR (CD_3SOCD_3): δ6·91–7·43 (3 d's, 8H, J = 5·0 cs, thiophene protons), 4·67 (s, 1H, methylene proton), the OH-absorption exchanges but is in CD_3COCD_3 observable at δ = 4·00 (s), IR (KBr) OH-absorption at 3500 cm^{-1}. (Found: C, 58·27; H, 2·79; S, 34·74. $C_{18}H_{10}OS_4$ requires: C, 58·35; H, 2·71; S, 34·62%).

$\Delta^{7,7'}$-*Bi-cyclopenta*[1,2-b:4,3-b′]*dithiophene* (XXIII). To a boiling soln of XXII (108 mg; 0·29 mmole) in 20 ml AcOH was added 1 drop conc HCl. The warming mantle was removed immediately, so that the mixture cooled down slowly. In the red brown soln dark brown crystals appeared. After suction on a Büchner funnel and washing with AcOH and water the yield of the dried product was 51 mg, while from the mother liquor a second crop (17 mg) could be obtained. Recrystallization from benzene gave 63 mg (61%) of XXIII as dark brown crystals with purple glow, m.p. 269–271°; IR 1315 (w), 705 (s), 750 (w) cm^{-1}. Mass spectrum: $m/e = 352$ (Found: C, 60·99; H, 2·34; $C_{18}H_8S_4$ requires: C, 61·33; H, 2·28%).

7,7′-7′H-*Cyclopenta*[1,2-b:4,3-b′]*dithiophene*-7H-*cyclopenta*[1,2-c:3,4-c′]*dithiophene-7-ol* (XXV). The reaction was carried out as for XXII with the exception that 356 mg (2·0 mmole) 7*H*-cyclopenta[1,2-*c*:3,4-*c′*]-dithiophene-7-one[9] was dissolved in 20 ml ether-THF 1:1 instead of only ether. After two crystallizations from CCl_4 and one from a mixture of benzene-light petroleum (60–80°) the yield on XXV was 55%, dec 185–206; NMR (CD_3COCD_3): δ 4·67 (d, 1H, J = 0·6 c/s, methylene proton), δ 5·39 (s, 1H, OH), δ 6·84 (d, 2H, H_1 and $H_{6'}$, J = 2·0 c/s), δ 7·30 (dd, 2H, $H_{2'}$ and $H_{5'}$, J = 5·0 c/s and J = 0·6 c/s); δ 7·15 (d, 2H, H_3 and H_4, J = 2·0 c/s), δ 7·03 (d, 2H, $H_{3'}$ and $H_{4'}$, J = 5·0 c/s); IR (KBr) OH-absorption at 3307 cm^{-1}. (Found: C, 58·47; H, 2·79; S, 34·43. $C_{18}H_{10}OS_4$ requires: C, 58·35; H, 2·71; S, 34·62%).

$\Delta^{7,7'}$-*Cyclopenta*[1,2-c:3,4-c′]*dithiophene-cyclopenta*[1,2-b:4,3-b′]*dithiophene* (XXVI). A soln of XXV (95 mg; 0·26 mmole) in 10 ml AcOH was warmed at 80° after which 1 drop of conc HCl was added. The soln immediately coloured orange red and after a few min crystals appeared. After warming for 10 min at 80° the mixture was cooled and the crystals were removed by filtration. After washing with AcOH and water the crystals were dried. One crystallization from benzene-petrol (60–80°) did not change the mp (248–249°) of these beautiful orange brown crystals. The yield was 68 mg (76%); IR 1613 (w), 1320, 1335, 1362 (w), 712 (s), 730 (s), 777 (s) cm^{-1}. (Found: C 60·97; H, 2·30; S, 35·84. $C_{18}H_8S_4$ requires: C, 61·33; H, 2·28; S, 36·39%).

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