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Synthesis of 2,3-, 2,5-, and 2,6-Disubstituted-Benzobarrelenes High Temperature Bromination II

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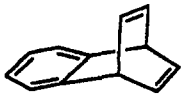
Abstract: Bromination of 2-bromo-1,4-dihydro-1,4-ethenonaphthalene (**7**) at -0 °C has been found to give five rearranged tribromides **8, 9, 10, 11,** and **12** via Wagner-Meerwein rearrangement with accompanying aryl and alkyl migration. It has been shown that the endo tribromides **9** and **11** are secondary products formed by bromine-catalyzed reaction of the corresponding exo tribromides. The bromination of **7** at 78 °C resulted in the formation of the non-rearranged products **21, 22, 23,** and **24** with bicyclo-[2.2.2]skeleton.The structure of **8, 10, 11** and **21** have been determined by X-ray structural analysis. The dehydrobromination of the tribromides **21, 22, 23,** and **24** with potassium tert-butoxide provided the corresponding benzobarrelenes **2a, 3a,** and **4a** in high yield. Reaction of dibromobenzobarrelenes with CuCN resulted in the formation of dicyano derivatives **2b, 3b,** and **3b.** Reaction of **3a** with BuLi and subsequent quenching wih MeI afforded dimethyl derivative **3c.**

Introduction

The effect of substituents on the course of the di-π–methane rearrangement[1] of bicyclic compounds has been investigated in detail by Paquette and Bender[2]. Benzobarrelene **1** is an intriguing compound in view of the di-π-methane rearrangement. The symmetry of the parent hydrocarbon **1** ensures that there are two possible bridging modes. However, monosubstitution in a vinyl location increases the bridging-modes from two to six di-π-methane rearrangement. In view of this aspect substituted benzobarrelene derivatives are important compounds which can provide information about which bridging will be preferred and how the substituents will influence the reaction modes. For this reason, we were interested in the synthesis of mono-, di-, and trisubstituted benzobarrelene derivatives. Recently, we developed a



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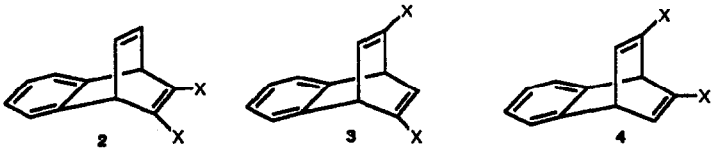
c) Author to whom inquires concerning the X-ray structure should be directed.

synthetic methodology leading to mono-[3] and 2,3-disubstituted[4] benzobarrelenes based on rearrangement of benzo[3.2.1]octene system into benzo- [2.2.2]octene systems. This rearrangement was performed by electrophilic addition of bromine to the double bond of benzo [3.2.1]octene system.

In a continuation of our investigation of the electrophilic addition of bromine to bicyclic systems, we report on the addition of bromine to 2-bromobenzobarrelene **7** and synthesis of 2,3-, 2,5-, and 2-6-disubstituted benzobarrelenes (**2,3, and 4**)[5] that have potential importance to explore the effect of the different substituent in the same molecule, on the course of the di-π-methane rearrangement.



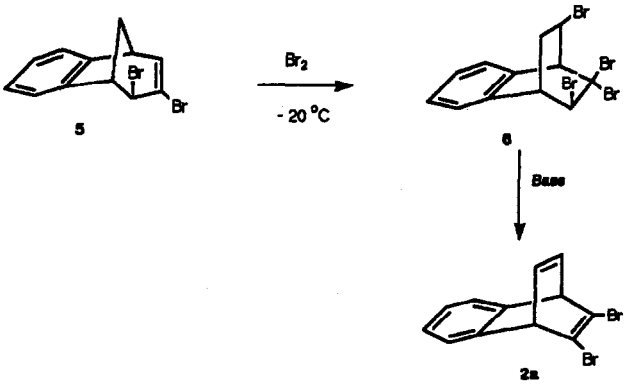
2 **3** **4**

a) X = Br
b) X = CN
c) X = CH_3

Results and Discussion

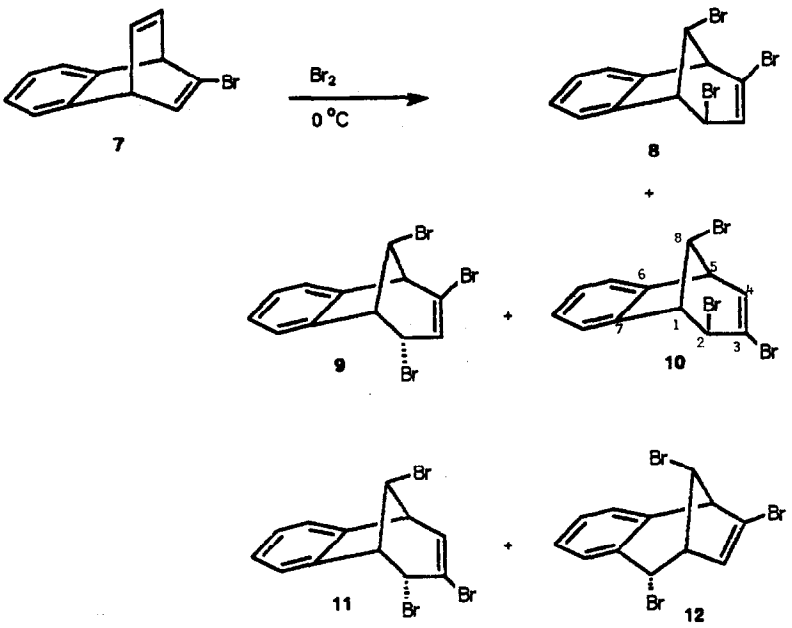
For the synthesis of 2,3-dibromobenzobarrelene[4] **2a** we submitted **5** to bromination. We have observed that the product distribution in the bromination reaction of **5** is dependent strongly on the reaction temperature. Therefore, we studied the bromination of **5** at different temperatures and found out that the bromination in dichloromethane solution at -20 °C, led to **6** in quantitative yield. The double dehydrobromination of **6** was achieved by using potassium *tert*-butoxide (Scheme I). For the synthesis of **3** and **4** we used 2-bromobenzobarrelene **7** as the starting material. Addition of bromine to the unsubstituted double bond in **7** giving unrearranged products, followed by HBr elimination should give a mixture of **3a** and **4a**. For this

Scheme I



reason we reacted **7** with bromine at 0 °C. The starting material **7** was prepared by our published method[3a] starting from benzonorbornadiene and was subjected in pentane at 0 °C to bromination. The ^{1}H-NMR studies revealed that the reaction mixture was very complex and consisted of five products. The reaction mixture was crystallized from pentane and we isolated as the major product **8** in a yield of 58 %. The rest was subjected to repeated column chromatography and we isolated 4 additional products **9, 10, 11,** and **12** in a yield of 19, 3, 6, and 9 %, respectively (Scheme II). The structure of the products has been elucidated on the basis of spectral data obtained by ^{1}H-NMR (400 MHz), and ^{13}C-NMR experiments. We don't intend to discuss all the spectra separately, but, we wish to discuss only ^{1}H-NMR spectrum of

Scheme II



the compound **10**. The aromatic protons resonate at δ 7.15-7.39 as multiplet. The olefinic proton gives rise to triplets of doublet. The doublet splitting (J = 7.0 Hz) originates from the bridge head proton H_5 and triplet splittings from the allylic proton H_2 and bridge proton H_8, respectively. Bridge proton H_8 is resonating at 4.69 as doublets of triplet. Bridgehead protons appear at 3.98 as doublet (H_1) and at 3.71 as doublets of doublet (H_5). The proton adjacent to bromine gives rise to a triplet at 4.62 ppm. Generally, the exo-configuration of the bromine at C_8 in **8, 9, 10**, and **11** was determined on the basis of coupling constants between bridge proton H_8 and bridgehead protons H_1 and H_5. As a consequence of the rigid geometries and reliability of the Karplus rule[6] in bicyclo-[3.2.1]octane systems[7], the dihedral relationship of the C-5-H (C-1-H) bond to an endo- (20°) to an exo-proton (90°) are sufficiently distinctive to be releaved by the

magnitude of the spin-spin interactions. Thus, the high value of the J_{18} and J_{58} in **8, 9, 10,** and **11** (J = 4.0, 4.2 Hz) is uniquely accomodated by the exo-orientation. (endo-configuration of bromine) of H_8. The configuration of the bromine at C_4 (**8** and **9**) and C_2 (in **10** and **11**) was also determined from coupling constants J_{45} (in **8** and **9**) and J_{12} (in **10** and **11**), respectively. We observe a large coupling constant (J = 4.6 and J = 5.0 Hz for **9** and **11**) in the case of endo-orientation of bromine and a small coupling for exo-orientation (J = 1.2 and J < 0.7 Hz for **8** and **10**). Finally, X-ray structure analysis of **8**, **10**[8], and **11** (Figure 1 and Figure 2) confirmed these structural findings. Among the compounds we isolated an alkyl shift product **12** whose ^{1}H-NMR and ^{13}C-NMR were completely in agreement with the proposed structure.

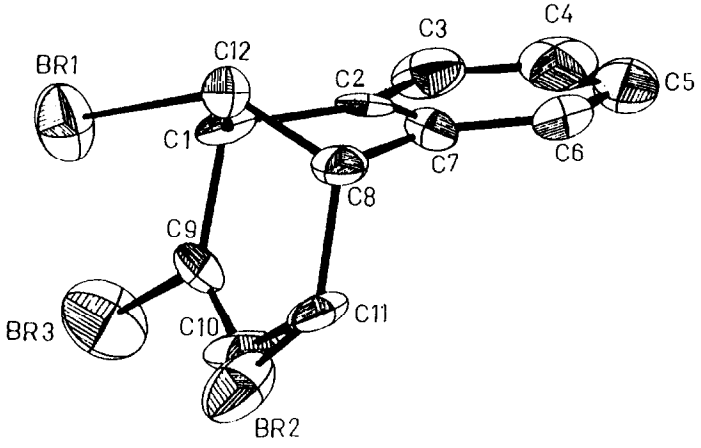


Figure 1. X- Ray Crystal Structure of 8.

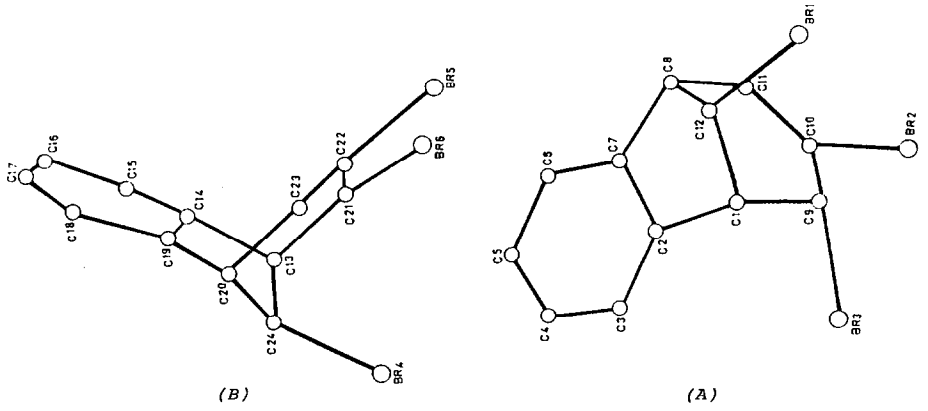
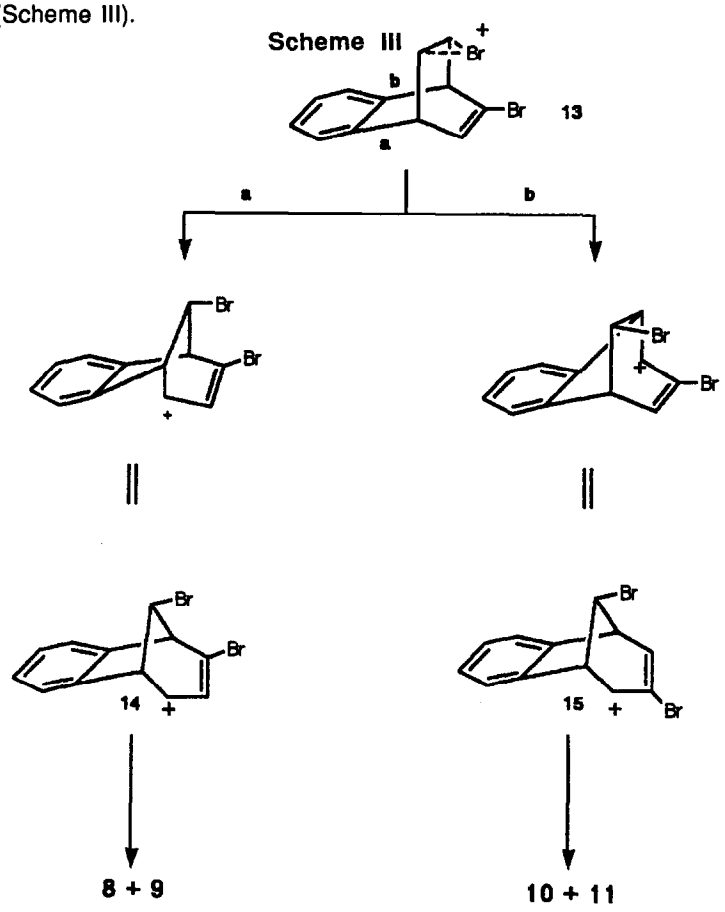


Figure 2. X- Ray Crystal Structure of 11.

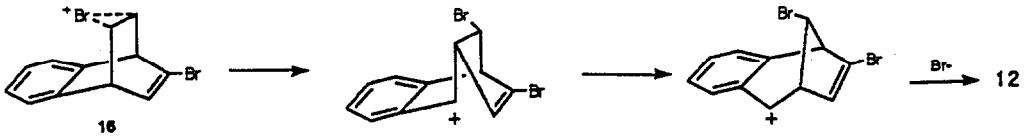
Structural determination of these compounds have revealed that the desired non-rearranged products were not formed even in traces which could be precursors for **3** and **4**. For the formation of the rearranged products we proposed following reaction mechanism. Product analysis indicates clearly that bromine has added only to the unsubstituted double bond in **7**. It is known that the bromine decreases the reactivity of the double bond towards electrophiles. Therefore it is not suprising that we have isolated only products arising from addition of bromine to the unsubstituted double bond. The bromine atoms bonded at bridge carbon (C_8) in all four isomers **8, 9, 10**, and **11** have the endo-configuration. It is evident from the bromine configuration at bridge carbon that initial attack by the bromine has occured from exo-face of the π-system. Most reasonably the driving force of this mode of addition is supplied by the formation of an aryl bridged intermediate. Since the exo-attack intermediate **13** is unsymmetrical, there are two possible aryl shifts involving aryl bonds "a" and "b". The fact that **8** was formed as the major product indicates that the shift of the aryl bond "a" is predominating which can be explained in turns of mesomeric effect of the bromine atom which increases the stability of the cation **14** over **15** (Scheme III).

Scheme III



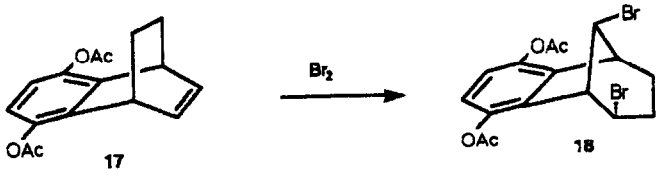
The formation of the alkyl shift product **12** can be explained in terms of the formation of the endo-intermediate **16** formed by endo attack of bromine to **7** (scheme IV). The determined endo-configuration of the bromine atom at the bridge carbon is also in agreement with the endo-attack. This intermediate is also unsymmetrical as in the case of **13**. Therefore one should also expect isomeric alkyl-shift products. But we were not able to isolate any other products beside **12** arising from alkyl-shift.

Scheme IV



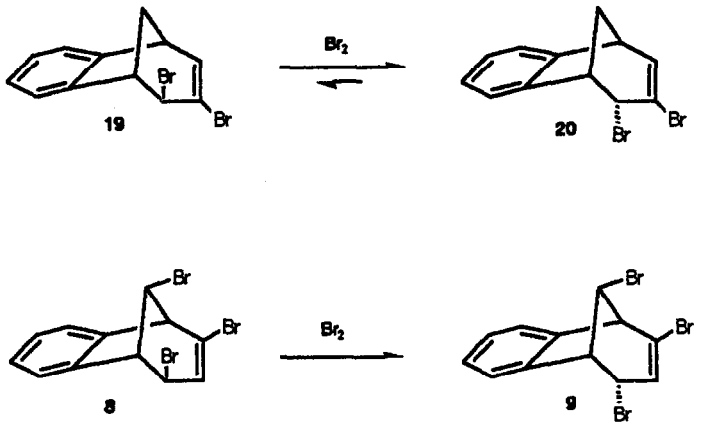
From the aryl shifts involving the aryl bonds "a" and "b" we isolated stereo isomers **8/9** and **10/11**. Recently, Smith et al.[9] and we[3a,b] have shown the formation of only one stereo isomer by addition of bromine to bicyclic systems. For example, the bromination of 5,8-diacetoxy-1,4-dihydro-1,4- ethanonaphthalene **17** has been found to give only one product **18** (Scheme V).

Scheme V



Therefore, we should obtain by this bromination reaction the exo-isomers **8** and **10**, according to the formation mechanism, not the isomers **9** and **11**. In the light of these results we believe that the isomers **9** and **11** are secondary products. Recently, we have discovered that the configuration isomerization of bromine[10] in the bicyclo[3.2.1]system can be catalyzed by molecular bromine. Treatment of a solution of the pure exo dibromide **19** with bromine in day light for 10 min. resulted in the formation of a equilibrium mixture consisting from exo and endo dibromides **19** and **20** (86:14) (Scheme VI). In analogy to this reaction we reacted the exo-bromide **8** with excess bromine and obtained in 45 min. endo tribromide **9** nearly in quantitative yield. Probably steric crowdness in **8** favor the formation of the endo tribromide **9**. Therefore, we assume that the formed endo-tribromides **9** and **11** are secondary products formed during bromination reaction.

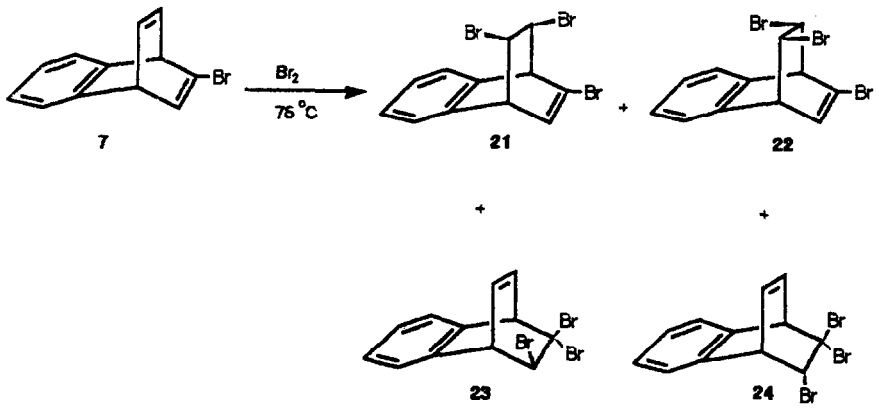
Scheme VI



In the course of studying bromination reaction we noticed that the reaction temperature has a dramatically influence on the product distribution. Increasing of the temperature gives non-rearranged reaction products[3b,4]. This fact encouraged us to go with the bromination temperature higher in order to trap the nonrearranged bromination products derived from **7**.

For this reason, we submitted **7** to high temperature bromination. To a refluxing solution of **7** in carbon tetrachloride was added a hot solution of bromine in carbon tetrachloride in one portion. The colour of bromine disappeared immediately. After silica gel chromatograpy followed by fractional crystallization we isolated four products **21, 22, 23,** and **24** with non-rearranged skeleton. (Scheme VII).

Scheme VII



The NMR spectra of these isomers reveal sufficient information to allow tentative assignments to be made. Resonances of the olefinic protons gave information which of the two double bonds was brominated. Because of the very close structural similarity we were not able to make a clear-cut differentiation between the isomers **21** and **22** on the basis of the spectral parameters[11]. Therefore, we carried out a X-ray crystal analysis of the isomer **21**. After this we assigned the correct structure of **22**. The product analysis has indicated that bromine has added to the both double bond in a ratio of approximately 1:1.

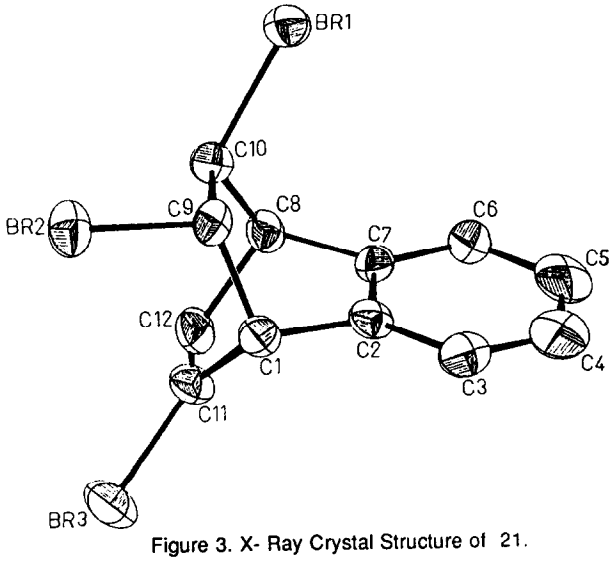
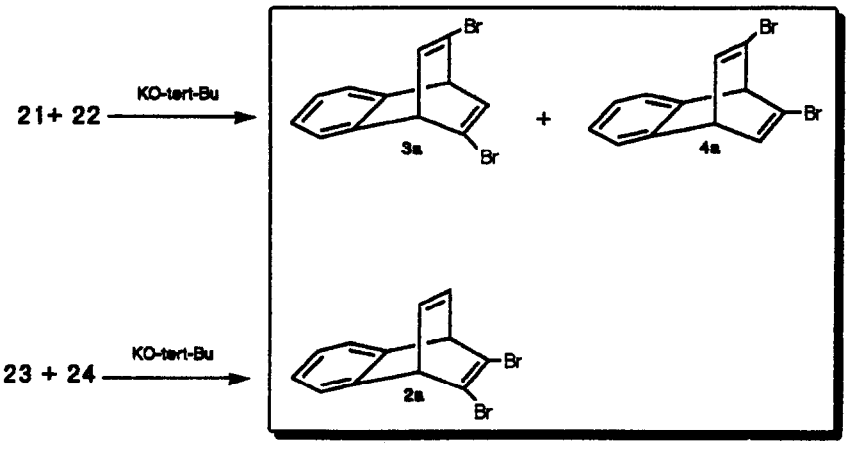


Figure 3. X- Ray Crystal Structure of 21.

Bromination reaction at 0 ^{o}C was completely regioselective. However, this regioselectivity was lost at high temperature. The formation of both stereo- isomers **21** and **22** (**23** and **24**) does not give any indication of which of the two competing modes of endo- and exo-attack is preferred, since both isomer pairs can be formed from endo-attack as well as from exo-attack. The different product distribution at 0 ^{o}C and 77 ^{o}C results from the life-time of the first formed intermediates exo- or endo-bromonium ion **13** and **16**. Since we increase the lifetime of these intermediates at 0 ^{o}C the rearrangement can take place completely. However, at 77 ^{o}C the bromine can attack the intermediates **13** and **16** before rearangement, since the lifetime is decreased. On the other hand, radical intermediates should be also considered by addition of bromine, since these are much less likely to rearrange.

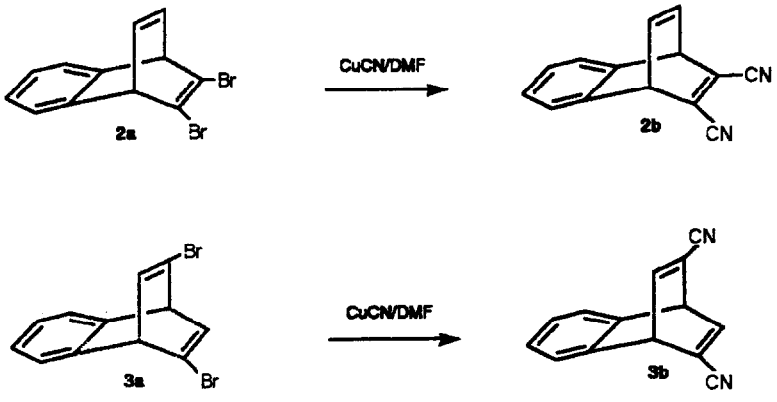
After succesfull synthesis of these desired isomers **21, 22, 23**, and **24**, the stage was now set for the critical cis-dehydrobromination of **21** and **22**. Treatment of a mixture consisting of **21** and **22** (or pure **21** and **22**) with potassium tert-butoxide proceeded with abstraction of the cis proton and cis elimination to give **3a** and **4a** in a ratio of 1:1 (80 %) which was separated by fractional crystallization (Scheme VIII).

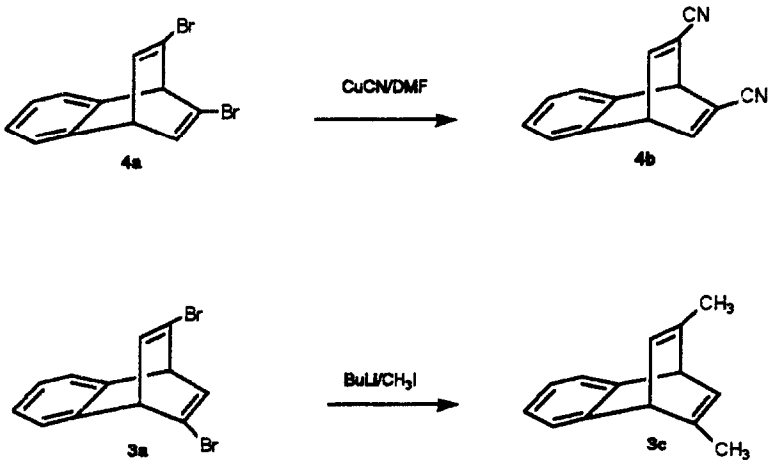
Scheme VIII



Structural assignments to **3a** and **4a** were achieved by means of proton and carbon NMR data. The ^{1}H- and ^{13}C-NMR spectra of **3a** were highly symmetrical according to the symmetry in the molecule. The ^{1}H-NMR spectrum consists of an AA'BB' system (aromatic protons) and a doublets of doublet arising from the bridgehead and double bond protons. A six-line ^{13}C-NMR spectrum is in good agreement with the proposed structure. The spectral data of **4a** are straigtforward for this structure. Especially a ten-line ^{13}C-NMR spectrum sports strongly the unsymmetrical structure. Dehydrobromination of a mixture consisting of **23**, and **24** which provides the configurational requirements for a trans dehydrobromination, provided **2a** in high yield (98%) (Scheme VIII). With the completion of the synthesis of our target molecules **2a, 3a,** and **4a** we opened up an entry to the other and at different position disubstituted benzobarrelene derivatives.

Scheme IX





At first we set out to determine if **3a** could be effectively dimetalated. When this dibromide was treated at -78 °C with an excess of n-butyllithium followed by methyliodine, dimethyl derivative **3b** was produced. **2a**, **3a**, and **4a** were heated with cuprous cyanide in dimethylformamide (DMF) at 130°C for several hours. The vinylic bromine atom was replaced in high yield (Scheme IX).

Experimental Section

General: Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1 mm cells or KBr pellets for solids on a Perkin-Elmer 337 Infrared recording spectrophotometer. The ^{1}H-NMR spectra were recorded on an EM 360 Varian, Brucker WM 300, 360 and 400 MHz spectrometer and are reported in δ units with $(CH_3)_4Si$ as internal standard. Apparent splittings are given in all cases. Mass spectra were recorded on a Finnigan-MAT MS Model 4000 mass spectrometer at an ionizing voltage 70 eV. All column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical alumina plates.

Bromination of 2-Bromo-5,6-benzobicyclo[2.2.2]octa-2,5,7-triene 7 at 0 °C. To a solution of 1.1 g (4.72 mmol) of 2-bromo benzobarrelene in 5 mL of chloroform was added 50 mL of pentane and cooled to 0 °C. To the resulting solution was added a solution of 760 mg (4.74 mmol) of bromine in 15 mL of pentane dropwise during 10 min. The solvent was removed under reduced pressure. The residue was crystallized from CH_2Cl_2/pentane (1:1) to give the exo-dibromide **8** (800 mg 46%).

exo,exo-2,4,8-Tribromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 8. Colorless clusters, mp 155-156 °C, ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0-7.5 (m, 4H, aryl), 5.85 (dt, $J_{13} = J_{35}$=

1.2 Hz, J_{34} = 3.8 Hz, 1H, H_3), 4.7 (t, $J_{18} = J_{58}$ = 4.2 Hz, 1H, H_8), 4.55 (dd, J_{45} = 1.2 Hz, 1H_4), 3.7-3.9 (m, 2H, H_1 and H_5); ^{13}C NMR (90 MHz, $CDCl_3$) ppm 146.33, 140.27, 128.44, 128.34, 126.72, 125.31, 124.33, 121.91, 56.27, 49.00, 47.41, 44.76; MS, (m/e, %) 390/392/394/396 (m^+, 9), 311/313/315 (M-Br, 55), 152/153 (M-2Br. 100); IR (KBr, cm^{-1}) 3060, 2980, 1620, 1410, 1320, 1290, 1240, 1160, 975.

After filtration of the tribromide **8**, the organic solvent was evaporated and the oily residue (950 mg) was subjected to silica gel (100 g) chromatography, eluting with petroleum ether. We isolated four products as well as tribromide 8. The first component isolated was identified as **9**.

endo,exo-2,4,8-Tribromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 9. (220 mg, 13 %): mp 97-98 °C, colorless crystals from chloroform-hexane; ^{1}H NMR (60 MHz, CCl_4) δ 7.0-7.3 (m, 4H, aryl), 5.6 (dt, 1H, H_3), 5.05 (dd, J_{45} = 4.6 Hz, J_{34} = 2.8 Hz, 1H, H_4), 4.5 (t, $J_{18} = J_{58}$ = 4.2 Hz, 1H, H_8), 3.3-3.6 (m, 2H, H_1 and H_5); ^{13}C NMR (90 MHz, $CDCl_3$) ppm 145.92, 138.49, 128.50, 127.65, 127.42, 125.36, 125.25, 121.59, 55.43, 53.63, 50.48, 47.65; IR (KBr cm^{-1}) 3060, 2960, 1620, 1465, 1320, 1235, 1100, 1150.

The second component proved to be **12**

endo,endo-2,7,8-Tribromo-3,4-benzobicyclo[3.2.1]octa-2,6-diene 12. (160 mg, 9 %), colorless needles, mp 111-112 °C from chloroform/hexane; ^{1}H NMR (60 MHz, CCl_4) δ 6.9-7.7 (m, 4H, aryl), 6.15 (d, J_{17} = 3.6 Hz, 1H, H_7), 5.65 (d, J_{12} =5 Hz, 1H, H_2), 4.85 (t, $J_{18} = J_{58}$ = 4.5 Hz, 1H, H_8), 3.4 (d, 1H, H_5), 3.3-3.5 (m, 1H, H_1); IR (KBr cm^{-1}) 3020, 2970, 1595, 1480, 1450, 1260, 1230, 1145, 1100, 910.

As the third fraction we isolated the tribromide **10**.

exo,exo-2,3,8-Tribromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene 10. (45 mg, 2.5 %); colorless needles, mp 125-126 °C from chloroform/n-hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.39 (m, 4H, aryl), 6.65 (dt, J_{45} = 7 Hz, 1H, H_4), 4.69 (td, $J_{18} = J_{58}$ = 4.2 Hz, 1H, H_8), 4.62 (t, J_{12} = 0, J_{42} = 1.2 Hz, H_2), 3.98 (d, H_1), 3.71 (dd, H_5); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 147.61, 139.82, 135.61, 128.28, 127.96, 124.63, 121.86, 120.29, 51.69, 50.51, 48.95, 46.42. MS(m/e, %) 390/392/394/396 (M^+, 8), 311/313/315 (M-Br, 50), 152/153 (M-3Br, 100); IR (KBr, cm^{-1}) 3060, 3040, 1610, 1465, 1330, 1280, 1235, 970.

As the last fraction we isolated the tribromide **11**.

endo,exo-2,3,8-Tribromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene 11. (70 mg, 4%) colorless crystals from chloroform/hexane, mp 147-148 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0-7.5 (m, 4H, aryl) 6.5 (d, J_{45} = 7 Hz, 1H, H_4), 5.15 (d, J_{12} = 5 Hz, 1H, H_2), 4.5 (t, $J_{18} = J_{58}$ = 4.0 Hz, 1H, H_8), 3.3-3.8 (m, H_1 and H_5); ^{13}C NMR (90 MHz, $CDCl_3$) ppm 146.68, 138.67, 134.52, 128.41, 127.66, 127.03, 121.49, 120.74, 53.65, 53.30, 48.36; MS (m/e, %) 390/392/394/396 (M^+, 7), 311/313/315 (M-Br, 52), 152-153 (M-3Br, 100); IR (KBr, cm^{-1}) 3060,

2990, 1610, 1470, 1460, 1240, 1210, 1170, 1150, 970.

Bromine-catalyzed Configuration Isomerization of exo-tribromide 8. To a solution of 30 mg (0.076 mmol) exo-tribromide **8** in 0.5 mL of $CDCl_3$ in a NMR tube was added 80 mg (0.5 mmol) bromine at room temperature. After 45 min ^1H NMR has revealed the configuration isomerization and the formation of **9** in quantitative yield.

Bromination of 2-Bromo-6,7-benzobicyclo[2.2.2]octa-2,6-diene 7 at 77 °C. 2-Bromobenzobarrelene **7** (1.2 g, 5.15 mmol) was dissolved in 40 mL of CCl_4 in a 100 mL flask which was equipped with reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added a hot solution (65-70 °C) of bromine (830 mg, 5.19 mmol) in 20 mL of carbon tetrachloride in one portion. The colour of bromine disappeared immediately. After being cooled to room temperature the solvent was evaporated. The oily residue was chromatographed on silica gel (170 g) eluting with hexane. The first component isolated was identified as **22**.

endo,exo-2,5,6-Tribromo-6,7-benzotricyclo[2.2.2]octa-2,6-diene 22. (280 mg, 14 %); colorless needles, mp 50-51 °C from chloroform/n-hexane); ^1H NMR (200 MHz, $CDCl_3$) δ 7.16-7.47 (m, 4H, aryl), 6.74 (dd, J_{34} = 6.35 Hz, J_{13} = 1.9 Hz, 1H, H_3), 4.43 (t, 1H, H_5), 4.22 (dd, J_{46} = 2.7 Hz, 1H, H_4), 4.16 (t, 1H, H_1), 3.99 (t, J_{56} = J_{16} = 2.85 Hz, 1H, H_6); ^{13}C NMR (50 MHz, $CDCl_3$) ppm 138.41, 136.97, 133.38, 127.51, 126.91, 126.42, 124.16, 123.73, 58.11, 54.42, 53.55, 50.73; MS (m/e, %) 390/392/394/396 (M^+, 6), 311/313/315 (M-Br, 17); (KBr, cm^{-1}) 3070, 3020, 2990, 1610, 1470, 1460, 1280, 1220, 1170, 1100. Anal. Calcd for $C_{12}H_9Br_3$: C, 36.71; H, 2.31; Br, 60.98. Found: C, 36.54; H, 2.27.

As second fraction we isolated the tribromide **21**.

exo,endo-2,5,6-Tribromo-6,7-benzotricyclo[2.2.2]octa-2,6-diene 21. (360 mg, 18 %); colorless needles, mp 127-128 °C from chloroform/n-hexane); ^1H NMR (60 MHz, CCl_4) δ 7.25 (s, 4H, aryl), 6.7 (dd, J_{34} = 6.8 Hz, J_{13} = 2.4 Hz, 1H, H_3), 4.33 (t, J_{64} = J_{65} = 2.6 Hz, 1H, H_6), 4.23 (t, 1H, H_5) 3.97 (t, 1H, H_1); MS (m/e, %) 390/392/394/396 (M^+, 8), 311/313/315 (M-Br); IR (KBr, cm^{-1}) 3000, , 2990, 1600, 1475, 1460, 1330, 1290, 1170, 1105. 980, 970.

The third component proved to be **23**.

exo-2,2,3-Tribromo-5,6-benzotricyclo[2.2.2]octe-2,6-diene 23. (200 mg, 10 %); mp 80-81 °C colorless needles from chloroform/n-hexane); ^1H NMR (60 MHz, CCl_4) δ 7.0-7.35 (m, 4H, aryl), 6.67 (m, 2H, H_5 and H_6), 4.78 (dd, J_{16} = 3.5 Hz, J_{15} = 2.5 Hz, 1H, H_1), 4.61 (d, J_{34} = 2.0 Hz, 1H, H_3) 4.24 (m, 1H, H_4); IR (KBr, cm^{-1}), 2990, 1600, 1550, 1475, 1460, 1290, 1170, 970. Calcd for $C_{12}H_9Br_3$: C, 36.71; H, 2.31; Br, 60.98. Found: C, 36.48; H, 2.38.

Lastly, endo tribromide **24** was isolated.

endo-2,2,3-Tribromo-5,6-benzotricyclo[2.2.2]octa-2,6-diene 24. (460 mg, 23 %); mp 109-110 °C colorless needles from chloroform/n-hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24-7.3 (m, 4H, aryl), 6.67 (m, 2H, H_5 and H_6), 4.96 (d, J_{34} = 2.4 Hz, 1H, H_3), 4.84 (dd, J_{16} = 4.7 Hz, J_{15} = 2.4 Hz, 1H, H_1), 4.14 (m, 1H, H_4); ^{13}C NMR (50 MHz, $CDCl_3$) ppm 139.22, 135.72, 135.64, 134.49, 126.95, 126.68, 126.27, 126.02, 66.11, 61.67, 59.69, 50.55; IR (KBr, cm^{-1}), 3060, 2990, 1640, 1550, 1475, 1460, 1250, 1180, 1105, 970. Calcd for $C_{12}H_9Br_3$: C, 36.71; H, 2.31; Br, 60.98. Found: C, 36.88; H, 2.40.

2,3-Dibromo-5,6-benzobicyclo[2.2.2]octa-2,5,7-triene 2a. To a solution of 60 mg (0.55 mmol) of sodium methoxide in 15 mL of dry and freshly distilled THF was added a solution of **23** or **24** (393 mg, 1 mmol) in 10 mL of dry THF while stirring magnetically. The resulting reaction mixture was refluxed for 3h. After being cooled to room temperature the solution was poured into a mixture of hexane (40 mL) and water (40 mL). The layers were separated and the aqueous phase was extracted with hexane. The combined organic layers were washed with water (2X40 mL), dried and evaporated to leave a pale yellow oil. The residue was purified by filtration through a short silica gel (5 g) column. Elution with hexane and crystallization from CH_2Cl_2/pentane (2:5) gave dibromobenzobarrelene **2a**. (302 mg, 95 %), mp 71-72 °C, colorless needles; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96-7.22 (AA'BB' system, 4H, aryl), 6.93 (X-part of AA'XX' system, H_5 and H_6), 4.95 (A-part of AA'XX' system, H_1 and H_4);^{13}C NMR (100 MHz, $CDCl_3$) ppm 144.54, 138.69, 129.41, 124.58, 122.61, 58.56; MS (m/e, %) 310/312/314 (M^+, 9), 231/233 (M-Br, 6), 152 (M-2Br, 100); IR (KBr, cm^{-1}), 1610, 1460, 1450, 1350, 1310, 1260, 1215, 1185, 1060, 980, 840, 755.

2,5-, and 2,6-Dibromo-7,8-benzobicyclo[2.2.2]octa-2,5,7-triene 4a and 3a. To a solution of 134 mg (1.2 mmol) of potassium tert-butoxide in 15 mL of dry and freshyl distilled THF was added a solution of **21** and **22** (393 mmol, 1mmol, 1:1) in 10 mL of dry THF while stirring magnetically. The resulting reaction mixture was refluxed for 3 h. After being cooled to room temperature, the solution was poured into a mixture of hexane (20 mL) and water (20 mL). The organic phase was washed with water, dried and rotoevaporated. The oily residue was subjected to a short silica gel (5g) column eluting with petroleum ether. The dibromobenzobarrelens **3a** and **4a** were separated by fractional crystallization. Firstly, 2,6-dibromobenzobarrelene **3a** was crystallized from methylene chloride/hexane (1:4) in refrigerator during one day. After filtration of **3a** the solvent was evaporated and the oily residue was crystallized from methylene chloride/pentane (1:6) in refrigerator to give **4a.**

2,6-Dibromo-7,8-benzobicyclo[2.2.2]octa-2,5,7-triene 3a. (110 mg, 35 %), colorless clusters; mp 172-173 °C(from methylene chloride/n-hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.91-7.16 (AA'BB' system, 4H, aryl), 6.83 (dd, J_{34} = J_{15}= 6.3 Hz, J_{45} = J_{13} = 2.4 Hz, 2H, H_3 and H_5), 4.68 (dd, 2H, H_1 and H_4); ^{13}C NMR (62.5 MHz, $CDCl_3$) ppm 144.48, 136.30,

132.44, 124.67, 122.77, 59.20; MS (m/e, %) 310/312/314 (M^+, 8), 231/233 (M-Br, 9), 206/208 (M-Br, -HC≡CH, 3); IR (KBr, cm^{-1}) 3010, , 2980, 1610, 1460, 1450, 1260, 1250, 1240, 1130. Anal. Calcd for $C_{12}H_8Br_2$: C, 46.23; H, 2.58; Br, 51.22. Found: C, 46.05; H, 2.41.

2,5-Dibromo-7,8-benzobicyclo[2.2.2]octa-2,5,7-triene 4a. (93 mg, 30 %): colorless needles, mp 101-102 °C(from methylene chloride/n-hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 6.94-7.3 (m, 4H, aryl), 6.84 (dd, $J_{34} = J_{64} = 6.27$ Hz, $J_{16} = J_{13} = 2.1$ Hz, 2H, H_3 and H_6), 4.76 (t, $J_{16} = J_{13} = 2.1$ Hz 1H, H_1), 4.76 (t, 1H, H_4); ^{13}C NMR (62.5 MHz, $CDCl_3$) ppm 144.59, 144.40, 136.80, 130.98, 125.12, 124.16, 123.15, 122,39, 51.27, 66.28; IR (KBr, cm^{-1}) 3070, 2980, 1580, 1460, 1450, 1260, 1200, 1190, 1130, 1090, 985. Anal. Calcd for $C_{12}H_8Br_2$: C, 46.23; H, 2.58; Br, 51.22. Found: C, 46.38; H, 2.64.

2,6-Dicyanobenzobarrelene 3b. A solution of 312 mg (1 mmol) of 2,6-dibromobenzobarrelene and 462 mg (2.58 mmol) of cuprous cyanide in 15 mL of dry DMF was stirred under nitrogen at at 130 °C for 10 h. The mixture was cooled, diluted with 200 mL of benzene and extracted with 5 % aqueous $FeCl_3$ (2X50 mL) then with 5% aqueous NaOH (2x50 mL) and finally with water (2x50 mL) . Organic layer was dried (magnesium sulfate) and concentrated in vacuum and the residue was purified by filtration through a short silica gel (5 g) column by eluting with chloroform/hexane (15:85). The residue was crystallized from THF/hexane. Colourless clusters (165 mg, 81%): mp 210-211 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.7-7.8 (dd, $J_{34} = J_{15} = 6.2$ Hz, $J_{45} = J_{13} = 2.0$ Hz, 2H, H_3 and H_5), 7.09-7.48 (AA'BB' system, 4H, aryl), 5.23 (dd, 2H, H_1 and H_4); ^{13}C NMR (75.0 MHz, $CDCl_3$) ppm 153.34, 141.43, 125.93, 124.16, 116.05, 51.29; MS (m/e, %) 204 (M^+, 100), 177 (60), 153 (69), 126 (34); IR (KBr, cm^{-1}) 3080, 2210, 1590, 1470, 1455, 1265, 1215, 1190, 895, 890, 760. Anal. Calcd for $C_{12}H_8N_2$: C, 82.35; H, 3.95; N, 28.01. Found: C, 82.27; H, 3.81.

The synthesis of 2,5- and 2,3-dicyanobenzobarrelenes was accomplished by the same experimental procedure as described above starting from the corresponding dibromobenzobarrelenes (1 mmol).

2,5-Dicyanobenzobarrelene 4b. (153 mg, 75%): mp 199-201 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.7 (dd, $J_{64} = 6.0$ Hz, $J_{61} = 1.6$ Hz, 2H, H_3 and H_6), 7.09-7.45 (m, 4H, aryl), 5.24 (t, 1H, H_4), 5.21 (t, 1H, H_1); ^{13}C NMR (75. MHz, $CDCl_3$) ppm 153.49, 142.06, 141.05, 126.06, 125.77, 124.91, 124.29, 124.01, 115.44, 52.66, 49.773 MS (m/e, %) 204 (M^+, 100), 177 (47), 153 (32), 126 (17); IR (KBr, cm^{-1}) 3090, 3080, 3045, 2225, 1590, 1470, 1465, 1455, 1265, 1270, 1130, 885. Anal. Calcd for $C_{12}H_8N_2$: C, 82.35; H, 3.95; N, 28.01. Found: C, 82.07; H, 4.01.

2,3-Dicyanobenzobarrelene 2b. (346 mg, 85% from 2 mmol **2a**): mp 155-156 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 7.20 (A-part of AA'XX' system, 2H, H_5 and H_6), 6.86 (AA'BB' system,

4H, aryl), 5.10 (X-part of AA'XX' system, 2H, H_1 and H_4); ^{1}IR (KBr, cm^{-1}) 3080, 3045, 3015, 2220, 1580, 1470, 1305, 1295, 1220, 1200, 1140, 1020. Anal. Calcd for $C_{12}H_8N_2$: C, 82.35; H, 3.95; N, 28.01. Found: C, 82.56; H, 3.72.

2,6-Dimethylbenzobarrelene 3c. To a solution of 2,6-dibromo benzobarrelene of 624 mg (2 mmol) in 15 mL of freshly distilled THF was added a solution of buthyl lithium (2.4 mmol, 3.6 mL) in hexane dropwise under a nitrogen atmosphere at -50 °C. The reaction mixture was stirred for an additional 15 min. At the same temperature was added a solution of CH_3I (320 mg, 2.2 mmol) in 5 mL of THF during 30 min. After allowing the reaction mixture to come to room temperature, a part of THF was removed under reduced pressure. To the resulting mixture were added 50 mL of water and 50 mL of petroleum ether and the combined organic layers were washed with water and dried. After removal of solvent, the oily residue was purified by filtration through a short (5g) silica gel column (290 mg, 80%). ^{1}H NMR (60 MHz, CCl_4) δ 6.7-7.3 (AA'BB' system, 4H, aryl), 6.25 (m, 2H, H_3 and H_5), 4.3 (dd, 2H, H_1 and H_4), 1.9 (d, 6H, CH_3); ^{1}IR (NaCl, cm^{-1}) 2960, 2925, 1460, 1440, 750.

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Table 1. Bond distances (A) and bond angles (o) of **8** with esd's in parentheses

Br1	C12	1.941(12)	C4	C5	1.385(23)
Br2	C11	1.976(13)	C5	C6	1.386(21)
Br3	C9	1.892(13	C6	C7	1.387(17)
C1	C2	1.522(18)	C7	C8	1.539(18)
C1	C9	1.514(18)	C8	C11	1.551(17)
C1	C12	1.503(18)	C8	C12	1.535(17)
C2	C3	1.382(19)	C9	C10	1.267(19)
C2	C7	1.381(19)	C10	C11	1.499(19)
C3	C4	1.378(22)			
H1	C1	1.069(13)	H8	C8	1.088(13)
H3	C3	1.105(15)	H10	C10	1.082(12)
H4	C4	1.086(16)	H11	C11	1.062(13)
H5	C5	1.066(15)	H12	C12	1.082(13)
H6	C6	1.073(15)			

C9	C1	C2	106.5(1.1)	C11	C8	C7	105.6(11)
C12	C1	C2	99.2(1.1)	C12	C8	C7	97.0(1.0)
C12	C1	C9	109.4(1.1)	C12	C8	C11	111.6(1.0)
C3	C2	C1	131.9(1.4)	C1	C9	Br3	116.2(1.0)
C7	C2	C1	107.6(1.2)	C10	C9	Br3	121.2(1.1)
C7	C2	C3	120.4(1.3)	C10	C9	C1	122.6(1.3)
C4	C3	C2	117.9(1.6)	C11	C10	C9	122.6(0.9)
C5	C4	C3	121.9(1.6)	C8	C11	Br2	112.6(0.9)
C6	C5	C4	120.5(1.4)	C10	C11	Br2	108.9(0.9)
C7	C6	C5	117.3(1.5)	C10	C11	C8	113.1(1.1)
C6	C7	C2	122.0(1.4)	C1	C12	Br1	113.7(0.9)
C8	C7	C2	109.9(1.1)	C8	C12	Br1	117.1(0.9)
C8	C7	C6	128.1(1.4)	C8	C12	C1	102.2(1.0)
H1	C1	C2	117.5(1.2)	H8	C8	C7	121.1(1.1)
H1	C1	C9	109.3(1.2)	H8	C8	C11	106.2(1.1)
H1	C1	C12	114.3(1.2)	H8	C8	C12	114.9(1.1)
H3	C3	C2	120.7(1.5)	H10	C10	C9	134.2(1.5)
H3	C3	C4	121.5(1.6)	H10	C10	C11	103.7(1.2)
H4	C4	C3	118.6(1.8)	H11	C11	Br2	111.0(0.9)
H4	C4	C5	119.6(1.7)	H11	C11	C8	104.0(1.1)
H5	C5	C4	117.5(1.6)	H11	C11	C10	107.2(1.2)
H5	C5	C6	122.0(1.6)	H12	C12	Br1	99.0(0.8)
H6	C6	C5	121.2(1.3)	H12	C12	C1	114.9(1.1)
H6	C6	C7	121.5(1.5)	H12	C12	C8	110.5(1.0)

Table 2. Bond distances (A) and bond angles (o) of **21** with esd's in parentheses

Br1		C10	1.967(9)	C4		C5	1.363(16)
Br2		C9	1.944(8)	C5		C6	1.404(14)
Br3		C11	1.866(9)	C6		C7	1.376(12)
C1		C2	1.520(13)	C7		C8	1.519(12)
C1		C9	1.553(12)	C8		C10	1.543(12)
C1		C11	1.555(12)	C8		C12	1.526(12)
C2		C3	1.394(2)	C9		C10	1.552(11)
C2		C7	1.405(12)	C11		C12	1.311(13)
C3		C4	1.390(15)				

C9	C1	C2	105.6(7)	C10	C8	C7	108.7(7)
C11	C1	C2	108.1(7)	C12	C8	C7	108.9(7)
C11	C1	C9	104.6(7)	C12	C8	C10	103.4(7)
C3	C2	C1	126.5(9)	C1	C9	Br2	111.2(6)
C7	C2	C1	113.4(7)	C10	C9	Br2	110.3(6)
C7	C2	C3	120.0(9)	C10	C9	C1	108.9(7)
C4	C3	C2	117.9(1.0)	C8	C10	Br1	110.4(6)
C5	C4	C3	122.2(9)	C9	C10	Br1	109.0(6)
C6	C5	C4	120.5(1.07	C9	C10	C8	109.9(7)
C7	C6	C5	118.3(1.0)	C1	C11	Br3	118.9(7)
C6	C7	C2	121.2(8)	C12	C11	Br3	126.0(0)
C8	C7	C2	112.1(7)	C12	C11	C1	115.0(8)
C8	C7	C6	126.7(8)	C11	C12	C8	113.7(8)
H1	C1	C2	112.6(8)	H8	C8	C7	108.5(7)
H1	C1	C9	113.6(7)	H8	C8	C10	113.8(7)

H1	C1	C11	118.(7)	H8	C8	C12	113.3(6)
H3	C3	C2	120.4(1.0)	H9	C9	Br2	108.1(6)
H3	C3	C4	121.7(9)	H9	C9	C1	109.2(7)
H4	C4	C3	118.3(1.1)	H9	C9	C10	109.2(7)
H4	C4	C5	119.5(1.1)	H10	C10	Br1	110.1(6)
H5	C5	C4	120.4(1.0)	H10	C10	C9	109.6(7)
H5	C5	C6	119.2(1.1)	H10	C10	C9	109.6(7)
H6	C6	C5	121.0(1.0)	H12	C12	C8	123.4(9)
H6	C6	C7	120.7(9)	H12	C12	C11	122.8(9)

Table 3. Bond distances (A) and bond angles (o) of **11** with esd's in parentheses

Molecule A			Molecule B		
C1	C2	1.491(14)	C13	C14	1.522(17)
C1	C9	1.564(11)	C13	C21	1.576(11)
C1	C12	1.588(12)	C13	C24	1.549(13)
C2	C3	1.448(15)	C14	C15	1.356(17)
C2	C7	1.43(14)	C14	C19	1.378(16)
C3	C4	1.294(18)	C15	C16	1.298(18)
C4	C5	1.339(24)	C16	C17	1.471(22)
C5	C6	1.405(20)	C17	C18	1.323(20)
C6	C7	1.366(15)	C18	C19	1.509(13)
C7	C8	1.558(14)	C19	C20	1.425(16)
C8	C11	1.555(15)	C20	C23	1.522(16)
C8	C12	1.500(15)	C20	C24	1.556(16)
C9	C10	1.472(13)	C21	C22	1.528(14)
C9	Br3	1.959(8)	C21	C22	2.005(11)
C10	C11	1.292(16)	C22	C23	1.323(157
C10	Br2	1.898(8)	C22	Br5	1.916(8)
C12	Br1	1.918(7)	C24	Br4	1.934(8)

Molecule A		Molecule B	
C2 - C1 - C9	112.6(7)	C14 - C13 - C21	112.2(8)
C2 - C1 - C12	96.1(7)	C14 - C13 - C24	99.7(8)
C9 - C1 - C12	107.2(6)	C21 - C13 - C24	105.6(7)
C1 - C2 - C3	131.8(9)	C13 - C14 - C19	106.8(1.0)
C1 - C2 - C7	113.2(8)	C15 - C14 - C19	121.2(1.0)
C3 - C2- C7	114.7(9)	C14 - C15- C16	121.6(1.1)
C2 - C3 - C4	119.7(1.1)	C15 - C16 - C17	120.2(1.0)
C3 - C4 - C5	125.7(1.2)	C16 - C17 - C18	121.5(9)
C4 - C5 - C6	119.2(1.1)	C17 - C18 - C19	116.0(1.1)
C5 - C6 - C7	117.8(1.1)	C14 - C19 - C18	118.7(1.1)
C2 - C7 - C6	122.8(9)	C14- C19 - C20	114.1(9)
C2 - C7 - C8	104.3 (8)	C18 - C19 - C20	127.1(1.0)
C6 - C7 - C8	132.(9)	C19 - C20 - C23	109.6(9)
C7 - C8 - C11	103.5(9)	C19 - C20 - C24	98.3(9)
C7 - C8 - C12	101.2(8)	C23 - C20 - C24	104.7(7)
C11 - C8 - C12	108.8(8)	C13 - C21 - C22	111.0(8)
C1 - C9 - C10	112.4(7)	C13 - C21 - Br6	107.5(6)
C1 - C9 Br3	105.9	C22 - C21 - Br6	108.6(6)

C10 - C9 - Br3	115.5(8)	C21 - C22 - C23	122.5(8)
C9 - C10 - Br2	113.2(7)	C21 - C22 - Br5	113.9(7)
C11 - C10 - Br2	121.2(7)	C23 - C22 - Br5	121.9(7)
C8 - C11 - C10	120.1(8)	C20 - C23 - C22	121.8(8)
C1 - C12 - Br1	102.6(8)	C13 - C24 - C20	101.7(7)
C1 - C12 - Br1	115.2(6)	C13 - C24 - Br4	115.5(6)
C8 - C12 - Br1	116.5(6)	C20 - C24 - Br4	118.5(7)
H1- C1 - C2	115.0(7)	H13 - C13 - C14	113.1(8)
H1 - C1 - C9	105.7	H13 -C13 - C21	108.0(8)
H1 - C1 - C12	120.1(8)	H13 - C13 - C24	118.8(9)
H3 - C3 - C4	120.0(1.1)	H15 - C15 - C14	119.2(1.0)
H3 - C3 - C2	120.3(1.1)	H15 - C15 - C16	119.1(9)
H4 - C4 - C3	117.1(1.3)	H16 - C16 - C15	120.0(1.1)
H4 - C4 - C5	117.2(1.1)	H16 - C16 - C17	119.8(1.1)
H5 - C5 - C4	120.2(1.2)	H17 - C17 - C16	119.3(1.2)
H5 - C5 - C6	120.6(1.5)	H17 - C17 - C18	119.2(1.5)
H6 - C6 - C5	121.2(1.1)	H18 - C18 - C17	121.9(9)
H6 - C6 - C7	121.0(1.1)	H18 - C18 - C19	122.0(1.1)
H8 - C8 - C7	118.0(9)	H20 - C20 - C19	115.0(9)
H8 - C8 - C7	118.0(9)	H20 - C20 - C19	115.0(9)
H8 - C8 - CC11	111.1(8)	H20 - C20 - C23	109.4(1.0)
H8 - C8 - C12	113.3(1.0)	H20 - C20 - C24	118.9(9)
H9 - C9 - C1	109.3(7)	H21 - C21 - C13	1355.7(9)
H9 - C9 - C10	138.4(8)	H21 - C21 - C22	111.3(7)
H9 - C9 - Br3	49.5(9)	H21 - C21 - Br6	45.8(4)
H11 - C11 - C8	137.5(9)	H23 - C23- C20	137.5 (9)
H11- C11 - C10	97.7(9)	H23 - C23 - C22	97.6(8)
H12 - C12 - C1	113.2(7)	H24 - C24 - C13	114.2(8)
H12 - C12 - C8	111.9(8)	H24 - C24- C20	116(8)
H12 - C12 -Br1	98. (5)	H24 - C24 - Br4	95.9 (5)

Table 4. Experimental data and structure refinement parameters.[12]

Compound	8	11	21
Formula	$C_{12}H_9Br_3$	$C_{12}H_9Br_3$	$C_{12}H_9Br_3$
Crystal shape	Rod-shaped	Rod-shaped	Prismatic
Number and range of reflections used for measuring lattice parameters	25 reflections with $28^o < 2\theta < 42^o$	25 reflections with $20^o < \theta < 44^o$	25 reflections with $30^o < 2\theta < 40^o$
Range of h, k and l	0 h 36, 0 k 12 0 l 11	-1 h 12, -11 k 11 -18 l 18	0 h 9, 0 k 11
Number or reflections measured	2240	5734	2167
Number of unique refl.	1480	4711	1295
Number of unobserved refl.	265	331	0
Criterion for recognizing unobserved reflections	$I < 3\sigma(I)$	$I < 3\sigma(I)$	$I < 3\sigma(I)$
Method used to solve structure	Direct method	Direct method	Patterson method
Use of F or F^2 magnit. in leastsquares ref.	F	F	F
Parameters refined	136	271	136
Values or R, R,ωR(int)	0.052, 0.052, 0.00	0.055	0.043, 0.043, 0.048
Final residual electron density for max. and min. peaks	±2.09 and -2.09	±2.08 and -0.70	±0.98 and -1.36
Source of atomic scattering factors	International tables for X-ray Crystallography 1974.		

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