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Syntheses and Spectral Properties of Norbornadiene-Fused Heterocycles: 1,3-Diphenyl-4,7-dihydro-4,7-methanobenzo[*c*]thiophene, -4,7-methano-2*H*-isoindole, and -4,7-methanoisobenzofuran

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The syntheses of a novel diphenyl-substituted thiophene, pyrrole, and furan fused at the 3- and 4-positions with norbornadiene are described. Structures of these molecules are discussed on the basis of spectral properties by comparison with those of cyclohexene-fused derivatives. Single crystal X-ray structural analysis of the norbornadiene-fused thiophene as well as the PM3 calculations of the related compounds revealed that the bond angles of carbon atoms at the ring-junction of norbornadiene-fused heterocycles are distorted.

Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) has been well-known to have considerably smaller bond angles on the sp^3 and sp^2 carbons than the normal angles.[1—3] The fusion of a norbornadiene framework, onto an aromatic ring is expected to cause distortion of the bond angles of the molecule and bond alternation due to the ring strain.[4,5] Therefore, it would be worthwhile to prepare such molecules and to study their physical and chemical properties including the possible through-space interaction between the aromatic ring and the ethylene moiety. For this purpose, extensive studies have been performed on 1,4-dihydro-1,4-methanonaphthalene (benzonorbornadiene) derivatives. These studies include analyses of their NMR[6—9] and photoelectron[10,11] spectra, nitration,[12] and photoreactions.[13] On the other hand, heteroaromatic analogues of benzonorbornadiene are a rare class of compounds. The syntheses and properties of norbornadiene-fused pyridines[14—17] and pyridazine[18] have been reported. As for the five-membered heteroaromatic analogues, the synthesis[19] and tranquilizing activities[20] of several 2-aryl-4,7-dihydro-4,7-methano-2*H*-isoindoles have been described without detailed spectral data. A polysubstituted 4,7-dihydro-4,7-methanobenzo[*b*]thiophene has been also reported.[21] However, unsubstituted 4,7-dihydro-4,7-methanobenzo[*b*]thiophene and -4,7-methano-1*H*-indole have been implicated only as transient intermediates in the reactions of cyclopentadiene with 2,3-didehydrothiophene[22] and 2,3-didehydropyrrole,[23] respectively. Attempts to prepare 4,7-dihydro-4,7-methanobenzo[*c*]thiophene[24,25] and -4,7-methanoisobenzofuran[26,27] have been unsuccessful. Thus, we planned the syntheses of diphenyl-substituted thiophene, pyrrole, and furan fused at the 3- and 4-positions with norbornadiene, expecting stabilization of the heteroaromatic rings by the phenyl substituents. In this paper, we wish to describe the successful syntheses of these derivatives, and discuss their spectral properties.

Results and Discussion

The treatment of *trans*-5,6-dibenzoylbicyclo[2.2.1]hept-2-ene[26] (**1**) with phosphorus pentasulfide in refluxing pyridine afforded 1,3-diphenyl-4,7-dihydro-4,7-methanobenzo[*c*]thiophene (**2**) albeit in a low yield (7%). The use of Lawesson's reagent could not improve the yield of **2**. The dibenzoylnorbornene **1** reacted with ammonium formate in refluxing ethanol to give 1,3-diphenyl-4,7-dihydro-4,7-methano-2*H*-isoindole (**3**) in 34% yield. It has been reported that the dibenzoylnorbornene **1** could not be converted to 1,3-diphenyl-4,7-dihydro-4,7-methanoisobenzofuran (**4**) on treatment with acetic acid or acetic anhydride–phosphoric acid.[26,27] Our attempts to prepare **4** by the reaction of **1** with acetic acid, sulfuric acid, or phosphorus pentaoxide also resulted in a complex mixture of products. It has been reported that triethyl phosphite is effective for the ring closure reaction of 2-butene-1,4-diones to furans.[28] Thus, we have chosen 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene[18] (**5**) as a potential precursor of the norbornadiene-fused furan **4**: Heating of dibenzoylnorbornadiene **5** with triethyl phosphite afforded the norbornadiene-fused furan **4** in 82% yield.

For the purpose of comparing spectral properties, 1,3-diphenyl-4,5,6,7-tetrahydrobenzo[*c*]thiophene (**7**) and -4,5,6,7-tetrahydro-2*H*-isoindole (**8**) were synthesized by the reactions of 1,2-dibenzoylcyclohexane[29] (**6**) with Lawesson's reagent and ammonium formate in 78 and 86% yield, respectively. 1,3-Diphenyl-4,5,6,7-tetrahydroisobenzofuran (**9**) was obtained by the reaction of **1** with sulfuric acid as described in the literature (Chart 1).[29]

The ^{1}H and ^{13}C NMR spectra of **2**—**4** show that these compounds have C_s symmetry. The ^{13}C NMR spectral data of the norbornadiene-fused heterocycles **2**—**4** and the cyclohexene-fused heterocycles **7**—**9** are summarized in Table 1 along with those of related compounds: benzonorbornadiene[9] **10**, 1,2,3,4-tetrahydronaphthalene[30] (**11**), 2,3-bis(methylene)bicyclo[2.2.1]hept-5-ene[31] (**12**), 1,2-bis(methylene)cyclohexane[32] (**13**), and 4,7-dihydro-4,7-methano-2*H*-indene[33] (**14**) (Chart 2). Unequivocal ^{13}C assignments were made with the help of selective proton-decoupled and/or COLOC (long-range H/C COSY) measurements. The

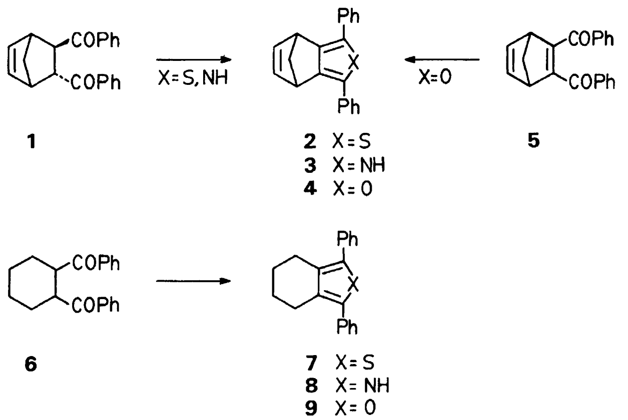


Chart 1.

^{13}C NMR signal of the C(b) carbon of the norbornadiene-fused thiophene **2** shows a large downfield shift ($\Delta\delta_{C(b)}=+15.2$) while that for the C(a) carbon shows an upfield shift ($\Delta\delta_{C(a)}=-5.8$), compared with the values of the corresponding carbons of the cyclohexene-fused thiophene **7**. Similar trends are observed for the ^{13}C chemical shifts of the pyrroles **3** and **8** ($\Delta\delta_{C(a)}=-2.2$, $\Delta\delta_{C(b)}=+17.1$), and of the furans **4** and **9** ($\Delta\delta_{C(a)}=-4.2$, $\Delta\delta_{C(b)}=+14.9$), as well as those of benzonorbornadiene **10** and tetrahydronaphthalene **11** ($\Delta\delta_{C(a)}=-8.2$, $\Delta\delta_{C(b)}=+14.3$). In contrast, the chemical shift of the C(b) carbon of bis(methylene)-norbornene **12** is similar ($\Delta\delta_{C(b)}=-1.4$) to that of bis(methylene)cyclohexane **13**, whereas the signal of the C(a) carbon of **12** shows an upfield shift ($\Delta\delta_{C(a)}=-7.2$). A systematic downfield shift of the ring-juncture carbons with increasing strain has been reported for benzocycloalkenes$^{34)}$ and their pyridine analogues,$^{35)}$ as well as fused cycloalkenes.$^{36)}$ Therefore, the downfield shift of the ring-juncture carbon, which is generally observed for the signals of the norbornadiene-fused heterocycles **2**—**4**, may be attributable, at least in part, to strain induced by a fused norbornadiene framework.

On the other hand, the ^{13}C chemical shifts for the C(c), C(d), and C(e) carbons in the norbornadiene-fused heterocycles **2**—**4** are comparable with those of benzonorbornadiene **10**. The signals of the C(e) carbons in **2**—**4** are deshielded when compared with those of **12** and **14**, in analogy with that of benzonorbornadiene **10**. The one-bond coupling constants ($^1J_{C-H}$) for the bridgehead C(c) carbons in **2**—**4** are slightly increased by 5—6 Hz relative to that of **12**. The results may be explained by a slight increase of s-character of the C–H bond, possibly due to an increase in strain by annelation with conjugated five-membered ring. The dihydromethanoindene **14**, a hydrocarbon analogue of **2**—**4**, also exhibits the comparable C–H coupling constant at the corresponding carbon.

The UV absorption patterns of the norbornadiene-fused thiophene **2** and pyrrole **3** are similar to those of the cyclohexene-fused analogues **7** and **8** (Table 2). However, the spectra of **2** and **3** display a slight but noticeable increase in the intensities with respect to those of **7** and **8**. An increase of absorption intensities with increasing strain has been reported for 3-thiabicyclo[3.2.0]hepta-1,4-diene vs. 3,4-dimethylthiophene,$^{37)}$ as well as benzocycloalkenes$^{38,39)}$ and their pyridine analogues.$^{35)}$ On the other hand, these features were not observed in the furan derivatives **4** and **9**. The UV data did not provide any information as to the existence of through-space interaction between the heteroaromatic ring and the ethylene moiety of the norbornadiene unit.

The norbornadiene-fused thiophene **2** was oxidized reversibly by a single-electron process with a half-wave potential of 1.01 V ($E^{1/2}$, vs. Ag/Ag$^+$ in acetonitrile). This value is slightly more positive by 60 mV than that of the cyclohexene-fused thiophene **7** ($E^{1/2}=0.95$ V). An increase of the oxidation potentials with increasing strain has been reported for fused naphthalenes.$^{40)}$

The X-ray crystal structure of the norbornadiene-fused thiophene **2** was determined. The crystal data and the final atomic coordinates are given in Tables 3 and 4. Selected bond distances, bond angles, and dihedral angles are shown in Table 5 along with bond distances and bond angles of **2** obtained by the MNDO-PM3 calculation$^{41)}$ and of thiophene obtained by microwave spectroscopy.$^{42)}$ ORTEP drawing and crystal structure for **2** are given in Figs. 1 and 2, respectively. A dominant feature drawn from the X-ray data is that the C(2)–C(3)–C(4) angle (139.6°) of **2** is distorted considerably from the value (123.28°) for thiophene. Further, the dihedral angle C(2)–C(3)–C(9)–C(7) (−176.0°) shows a slight deviation of the C(9)–C(7) bond toward *exo*-face from the thiophene plane. On the other hand, the values of other bond angles and bond distances in **2** agree with those of thiophene or norbornadiene$^{6)}$ within ±0.032 Å and ±2.1°. Table 5 shows that the PM3 calculation can reproduce the geometries of **2** with the deviations of 0.001—0.036 Å and 0.1—0.6° from those obtained with the X-ray analysis. The bond angles (α) of the norbornadiene-fused and the cyclohexene-fused heterocycles **15** and **16** obtained by the PM3 calculations are shown in Table 6 (Chart 3). The results also indicate distortion (ca. 15—16°) of the bond angles (α) in the norbornadiene-fused derivatives. Therefore, the changes of the ^{13}C NMR spectral properties in the norbornadiene-fused derivatives may be attributable to the angle-strain$^{43—45)}$ on the ring-juncture carbons.

We have discussed the spectral properties of norbornadiene-fused molecules **2**, **3**, and **4** with respect to those of the corresponding cyclohexene-fused systems because our main initial concern has been on the possibility of a through-space interaction between the remote double bond. The results presented above would support the view that an extra strain is incorporated into the heteroaromatic part of the molecule by intro-

Table 1. ^{13}C Chemical Shifts (ppm) and One-Bond Coupling Constants ($^1J_{C-H}$, Hz) of the Norbornadiene-Fused Heterocycles **2**—**4**, the Cyclohexene-Fused Heterocycles **7**—**9**, and Related Compounds **10**—**14**$^{a)}$

Compound	C(a) ($^1J_{C-H}$)	C(b)	C(c) ($^1J_{C-H}$)	C(d) ($^1J_{C-H}$)	C(e) ($^1J_{C-H}$)	Others
2	130.0	150.5	46.5 (151)	141.5 (174)	65.8 (137)	126.7, 127.0, 128.8, 134.3
7	135.8	135.3	27.0 (128)	23.4 (127)	—	126.9, 128.5, 128.6, 135.0
3$^{b)}$	124.3	135.6	44.8 (150)	142.2 (172)	69.1 (136)	124.3, 125.3, 128.5, 133.0
8$^{b)}$	126.5	118.5	23.8 (126)	23.5 (126)	—	124.8, 125.5, 128.2, 133.4
4	141.7	135.8	44.3 (150)	140.8 (174)	66.6 (137)	124.0, 126.6, 128.6, 131.5
9	145.9	120.9	23.3 (133)	23.0 (128)	—	124.6, 126.3, 128.5, 132.1
10	121.4	151.5	50.3 (148.5)	142.8 (174)	70.1 (135.5)	124.0
11	129.6	137.2	30.3	24.1	—	126.0
12	101.0	148.4	50.7 (145)	136.1 (171)	51.4 (135)	
13	108.2	149.8	35.6	27.1	—	
14$^{c)}$	114.8 (163)	154.7	44.0 (151)	138.3 (175)	59.3 (137)	47.0 (126)

a) Measured in $CDCl_3$ unless otherwise specified and the values of **10**—**14** are collected from references; b) in DMSO-d_6; c) in C_6D_6.

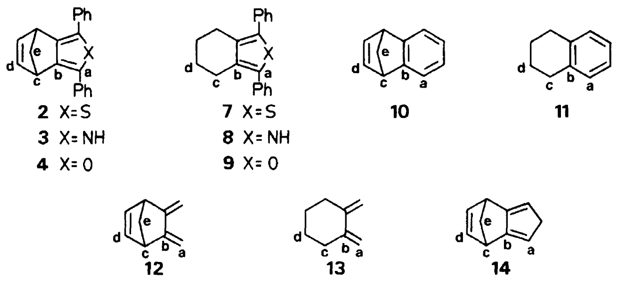


Chart 2.

duction of a methano bridge onto the cyclohexene unit in these molecular systems. However, for discussion of strain, it may appear more appropriate to regard these molecules as cyclopentene-fused heteroaromatics into which an etheno bridge is introduced. Unfortunately, paucity of existing data on suitable cyclopentene-fused model compounds has precluded discussion from this viewpoint.

Finally, in a hope to obtain a chemical criterion on the degree of delocalization on the heteroaromatic rings, the Diels–Alder reactions of the norbornadiene-fused thiophene **2**, pyrrole **3**, and furan **4** with dimethyl acetylenedicarboxylate (DMAD) or *N*-phenylmaleimide were tried. These attempted reactions at temperatures up to 180 °C resulted in the recoveries of starting materials. The failure to realize such reactions, however, may be due to steric rather than electronic effect because a pyrrole and a furan, fused to a bicyclo[2.2.2]octa-2,5-diene ring, have been reported to give the cycloadducts with DMAD.[46,47] In order to gain information concerning the π–π interaction, the norbornadiene-fused furan **4** was irradiated with a high-pressure mercury lamp through Pyrex filter in dichloromethane. This resulted in the formation of a complex mixture of products.

Experimental

General. All the melting points were recorded with a Yanagimoto hot-stage apparatus and uncorrected. IR spectra were obtained with a Hitachi 345 spectrometer. ^{1}H (90 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded with a JEOL-FX-90Q spectrometer. ^{1}H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were obtained with a Bruker AC-250 spectrometer. UV spectra were recorded with a Shimadzu UV-260 spectrometer. Mass spectra were taken with a Shimadzu GCMS-QP1000EX spectrometer operating in the electron impact mode with an ionizing energy of 70 eV. Elemental analyses were performed with a Perkin–Elmer Model 240 apparatus. Cyclic voltammograms were obtained with a BAS-100A electrochemical analyzer with Et_4NClO_4 (0.1 mol dm^{-3}) as supporting electrolyte, glassy carbon working electrode, Pt-wire counter electrode, and Ag/Ag$^+$ (0.01 mol dm^{-3} $AgClO_4$) reference electrode. The sweep rate was 500 mV s^{-1}. The half-wave potential of ferrocene (Fc^0/Fc$^+$) was 0.09 V under the same conditions.

X-Ray diffraction data were collected at room temperature by an ENRAF–NONIUS CAD4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.548$ Å). 3466 Reflections ($2\theta < 140°$) were measured using ω–2θ scan method, and 1640 independent reflections ($|F_o| > 3\sigma(F_o)$)

Table 2. The UV Data of the Norbornadiene-Fused Heterocycles **2**—**4**, and the Cyclohexene-Fused Heterocycles **7**—**9**

Compound	λ_{max} nm (ε) in EtOH
2	226 (10800), 265 (10600), 313 (26200)
7	236 (10600), 257 (8900), 310 (22700)
3	234 (11200), 272 (10400), 330 (34500)
8	238 (7300), 259 (5400), 332 (25000)
4	229 (18200), 255 (11200), 322 (36300), 335 (27000, sh)
9	235 (19100), 244 (18200), 330 (31600), 343 (21900, sh)

Table 3. Crystal Data for the Norbornadiene-Fused Thiophene **2**

Color	Colorless
Crystal shape	Needles
Crystal size/mm^3	0.15×0.15×0.35
Formula	$C_{21}H_{16}S$
F.W.	300.42
Cryst. syst.	Orthorhombic
Space group	$P2_12_12_1$
a/Å	14.240(1)
b/Å	18.870(2)
c/Å	5.800(1)
α/degree	90.0
β/degree	90.0
γ/degree	90.0
V/Å^3	1558.4(3)
Z	4
D_{calcd}/g cm^{-3}	1.28
μ/mm^{-1}	17.21
R	0.032
Rw	0.037

Table 4. Final Atomic Coordinates (×10^4) of Non-H Atoms for the Thiophene **2** and Equivalent Isotropic Thermal Parameters

Atom	x	y	z	$B_{eq}$$^{a)}$
S(1)	7561(0)	8126(0)	2993(1)	3.6
C(2)	8503(1)	8456(1)	1393(4)	3.2
C(3)	8980(1)	7908(1)	424(4)	3.2
C(4)	9862(2)	7774(1)	−1010(4)	3.6
C(5)	9498(2)	7436(1)	−3242(4)	4.3
C(6)	9163(2)	6798(1)	−2723(5)	4.2
C(7)	9272(2)	6688(1)	−119(4)	3.6
C(8)	10207(2)	7097(1)	239(4)	3.9
C(9)	8607(1)	7228(1)	966(4)	3.2
C(10)	7829(1)	7244(1)	2322(4)	3.3
C(11)	7246(1)	6666(1)	3268(1)	3.5
C(12)	6746(2)	6744(1)	5287(5)	4.5
C(13)	6189(2)	6200(2)	6124(6)	5.4
C(14)	6155(2)	5557(1)	4989(6)	5.7
C(15)	6655(2)	5469(1)	2992(6)	5.7
C(16)	7203(2)	6017(1)	2109(6)	4.7
C(17)	8683(1)	9225(1)	1265(4)	3.3
C(18)	8388(2)	9680(1)	2998(5)	4.2
C(19)	8573(2)	10406(1)	2852(6)	4.9
C(20)	9051(2)	10673(1)	985(5)	4.8
C(21)	9340(2)	10228(1)	−743(5)	4.9
C(22)	9157(2)	9504(1)	−625(5)	4.4

a) $B_{eq}=(4/3)\sum_i\sum_j \beta_{ij}\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

were used for the analysis. No absorption correction was applied. The structure was solved by the direct method with the program MULTAN 78.[48] The position of the hydrogen atoms were obtained from a difference Fourier map. The atomic parameters were refined by a block-diagonal least-squares procedure; $w^{-1}=\sigma(F_o)^2+(0.015|F_o|)^2$. Anisotropic temperature factors were used for refining the non-hydrogen atoms and isotemperature factors were adopted for the hydrogen atoms. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[49] The calculations were performed on a HITAC M-680H computer in the Computer Center of Institute for Molecular Science using the programs UNICS III[50] and ORTEP.[51] List of structure factors, anisotropic temperature factors for non-hydrogen atoms, and atomic parameters for hydrogen atoms have been deposited as Document No. 66039 at the Office of the Editor of Bull. Chem. Soc. Jpn.

5,6-Dibenzoylbicyclo[2.2.1]hept-2-one (**1**),[8] 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**5**),[18] 1,2-dibenzoylcyclohexane (**6**),[11] and Lawesson's reagent[52] were prepared by the procedures as described in the literatures.

1,3-Diphenyl-4,7-dihydro-4,7-methanobenzo[*c*]thiophene (2): A solution of the dibenzoylnorbornene **1** (4.53 g, 15 mmol) and phosphorus pentasulfide (4.00 g, 18 mmol) in anhydrous pyridine (50 cm^3) was refluxed for 4 h under nitrogen. Pyridine was removed in vacuo and the residue was dissolved in dichloromethane. The organic phase was successively washed with dil hydrochloric acid, aq $NaHCO_3$, and water prior to drying over Na_2SO_4. After removal of the solvent, the residue was separated by column chromatography (silica gel, benzene) and TLC (silica gel, hexane–ethyl acetate=10/1) to give the norbornadiene-fused thiophene **2** (313 mg, 7%) as colorless needles (from hexane–chloroform): Mp 172—173 °C; IR (KBr) 1660, 1480, 1305, 1075, 1020 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ=2.45 (2H, t, J=1.6 Hz, 8-H), 4.01 (2H, dq, J=2.0, 1.6 Hz, 4- and 7-H), 6.81 (2H, dd, J=2.0, 1.6 Hz, 5- and 6-H), 7.20—7.28 (2H, m, Ph), 7.32—7.40 (4H, m, Ph), 7.51—7.56 (4H, m, Ph); MS m/z (rel intensity) 300 (M$^+$, 100), 121 (17, PhCS). Found: C, 84.09; H, 5.53%. Calcd for $C_{21}H_{16}S$: C, 83.96; H, 5.37%.

1,3-Diphenyl-4,7-dihydro-4,7-methano-2*H*-isoindole (3): A solution of the dibenzoylnorbornene **1** (4.53 g, 15 mmol) and ammonium formate (3.79 g, 60 mmol) in ethanol (50 cm^3) was refluxed for 47 h. The mixture was concentrated, and benzene was added to the residue. The organic phase was washed with aq $NaHCO_3$ and water prior to drying over Na_2SO_4. After removal of the solvent, the residue was separated by column chromatography (silica gel,

Table 5. Selected Bond Distances (Å), Bond Angles (°), and Dihedral Angles (°) of the Norbornadiene-Fused Thiophene **2** and Thiophene

	2[a)]	**2**[b)]	Thiophene[c)]
Bond distance			
S(1)-C(2)	1.746(2)	1.771	1.714
C(2)-C(3)	1.360(3)	1.359	1.370
C(3)-C(4)	1.527(3)	1.510	
C(4)-C(5)	1.534(3)	1.527	
C(5)-C(6)	1.329(3)	1.347	
C(3)-C(9)	1.424(3)	1.460	1.423
C(4)-C(8)	1.550(3)	1.570	
Bond angle			
S(1)-C(2)-C(3)	109.4(2)	109.3	111.47
C(2)-C(3)-C(4)	139.6(2)	139.8	123.28
C(3)-C(4)-C(5)	104.5(2)	104.6	
C(4)-C(5)-C(6)	107.9(2)	108.0	
C(3)-C(4)-C(8)	98.2(2)	98.8	
C(4)-C(8)-C(7)	94.3(2)	93.8	
C(2)-S(1)-C(10)	93.1(1)	93.2	92.17
Dihedral angle			
C(2)-C(3)-C(4)-C(5)	−119.2(3)		
C(2)-C(3)-C(4)-C(8)	139.1(3)		
C(2)-C(3)-C(9)-C(7)	−176.0(2)		
C(2)-S(1)-C(10)-C(9)	0.6(2)		
C(3)-C(2)-C(17)-C(18)	−154.4(2)		

a) Obtained by X-ray analysis. b) Obtained by MNDO-PM3 calculation (precise option). c) Obtained by microwave spectroscopy, see Ref. 41.

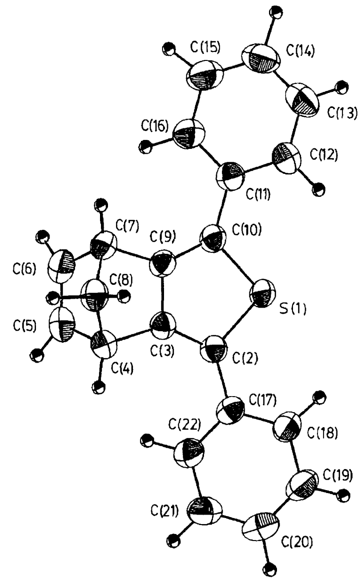


Fig. 1. ORTEP Drawing of the norbornadiene-fused thiophene **2** with the atomic numbering.

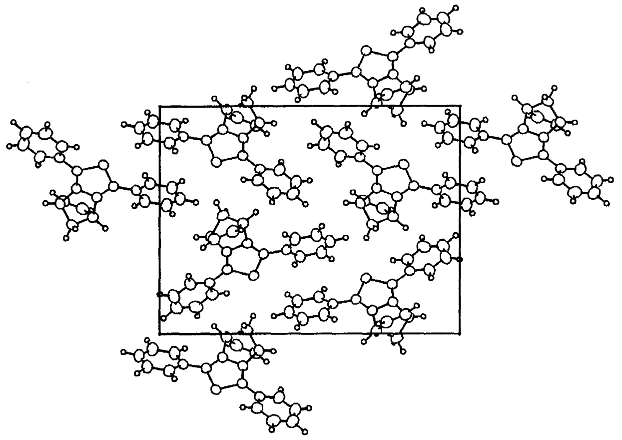


Fig. 2. Crystal structure of the norbornadiene-fused thiophene **2** viewed along the *c* axis.

benzene) to give the norbornadiene-fused pyrrole **3** (1.43 g, 34%) as colorless prisms (from hexane–chloroform): Mp 162—163 °C; IR (KBr) 3430 (NH), 2965, 1590, 1485, 1440, 1275 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ=2.34—2.57 (2H, m, 8-H), 4.07 (2H, tt, J=1.8, 1.5 Hz, 4- and 7-H), 6.79 (2H, t, 1.8 Hz, 5- and 6-H), 7.40—7.60 (11H, m, NH and Ph); MS m/z (rel intensity) 283 (M$^+$, 100). Found: C, 89.30; H, 6.02; N, 4.94%. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94%.

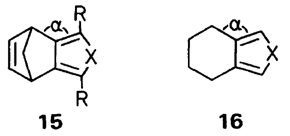
1,3-Diphenyl-4,7-dihydro-4,7-methanoisobenzofuran (4): A solution of the dibenzoylnorbornadiene **5** (11.36 g, 38 mmol) and triethyl phosphite (18.5 cm^3, 108 mmol) in anhydrous xylene (60 cm^3) was refluxed for 8 h under nitrogen. The solution was concentrated and methanol was added to the residue. The resulting crystals were collected by filtration to give the norbornadiene-fused furan **4** (8.82 g, 82%) as colorless needles (from ethanol): Mp 135—136 °C; IR (KBr) 3000, 2980, 2930, 2860, 1590, 1485, 1440, 1300, 1060, 830 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ=2.37 (2H, t, J=1.6 Hz, 8-H), 4.00 (2H, dt, J=1.8, 1.6 Hz, 4- and 7-H), 6.85 (2H, dd, 2.0, 1.8 Hz, 5- and 6-H), 7.10—7.50 (6H, m, Ph), 7.60—7.90 (4H, m, Ph); MS m/z (rel intensity) 284 (100, M$^+$), 105 (31, PhCO). Found: C, 88.70; H, 5.67%. Calcd for $C_{21}H_{15}O$: C, 88.55; H, 5.93%.

1,3-Diphenyl-4,5,6,7-tetrahydrobenzo[c]thiophene (7): A solution of the dibenzoylcyclohexane **6** (1.46 g, 5 mmol) and Lawesson's reagent (2.50 g, 6.3 mmol) in anhydrous pyridine (25 cm^3) was refluxed for 10 h. Pyridine was removed in vacuo and the residue was dissolved in toluene. The organic phase was washed with dil hydrochloric acid, aq NaHCO$_3$, and water prior to drying over Na$_2$SO$_4$. Toluene was removed in vacuo and the residue was crystallized from methanol to give the cyclohexene-fused thiophene **7** (1.14 g, 79%) as colorless needles (from hexane): Mp 86—87 °C; IR (KBr) 3060, 2935, 2865, 1590, 1480, 1430 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ=1.74 (4H, m, 5- and 6-H), 2.83 (4H, m, 4- and 7-H), 7.17—7.80 (10H, m, Ph); MS m/z (rel intensity) 290 (M$^+$, 100), 121 (12, PhCS). Found: C, 82.77; H, 6.52%. Calcd for $C_{20}H_{18}S$: C, 82.71; H, 6.25%.

1,3-Diphenyl-4,5,6,7-tetrahydro-2*H*-isoindole (8): A solution of the dibenzoylcyclohexane **6** (2.04 g, 7 mmol) and ammonium formate (4.41 g, 70 mmol) in ethanol (35 cm^3) was refluxed for 24 h. The mixture was concentrated, and toluene was added to the residue. The organic phase was washed with aq NaHCO$_3$ and dried over Na$_2$SO$_4$. Toluene

Table 6. Bond Angles (α, deg.) of the Norbornadiene-Fused and the Cyclohexene-Fused Heterocycles **15** and **16** Obtained by MNDO-PM3 Calculations

	Bond angle α (°)		
	15		**16**
	R=Ph	R=H	
X=S	139.8	140.8	125.1
X=NH	144.7	144.8	128.8
X=O	146.5	146.9	130.8



15 **16**

Chart 3.

was removed in vacuo and the residue was crystallized from methanol to give the cyclohexene-fused pyrrole **8** (1.66 g, 87%) as colorless needles (from ethanol): Mp 154—155 °C; IR (KBr) 3455 (NH), 2940, 1595, 1485, 1265 cm^{-1}; ^{1}H NMR (90 MHz, $(CD_3)_2SO$) δ=1.72 (4H, m, 5- and 6-H), 2.72 (4H, m, 4- and 7-H), 7.06—7.75 (10H, m, Ph), 10.82 (1H, br, NH); MS m/z (rel intensity) 273 (M$^+$, 100), 244 (87). Found: C, 87.97; H, 7.24; N, 4.85%. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12%.

1,3-Diphenyl-4,5,6,7-tetrahydroisobenzofuran (9): Colorless needles (from ethanol): Mp 98—99 °C (lit,[29] mp 97.5 °C); IR (KBr) 3100, 3060, 2950, 2870, 1610, 1600, 1490, 1440, 1120, 1070, 1040 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.60—2.00 (4H, m, 5- and 6-H), 2.60—3.00 (4H, m, 4- and 7-H), 7.00—7.56 (6H, m, Ph), 7.60—7.80 (4H, m, Ph); MS m/z (rel intensity) 274 (M$^+$, 100), 245 (25), 105 (19, PhCO). Found: C, 87.56; H, 6.61%. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.46%.

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