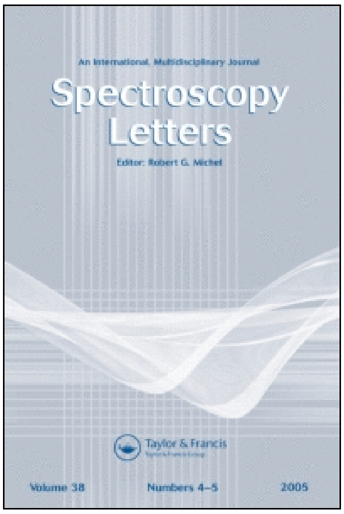

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Convenient Synthesis ^{1}H, ^{13}C NMR Study and X-Ray Crystal Structure Determination of Some New Disubstituted Thiophenes

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CONVENIENT SYNTHESIS ^{1}H, ^{13}C NMR STUDY AND X-RAY CRYSTAL STRUCTURE DETERMINATION OF SOME NEW DISUBSTITUTED THIOPHENES

Key Words :Thienylenediacrylic acids, ^{1}H and ^{13}C NMR spectra, synthesis, crystal structure

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ABSTRACT

2,5-, 3,4- and 2,3-Thienylenediacrylic (**1**, **4** and **7** respectively) were synthesized in one step reaction by catalytic vinylation of the corresponding dibromothiophenes in the presence of cyclohexylamine salt of acrylic acid. 2,4-Thienylenediacrylic acid **10** was prepared by catalytic vinylation of 3-(4-bromo-2-thienyl)acryilic acid.

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* correspondence and reprints

From **1**, **4**, 7 and **10**, the acid dichlorides **2**, 5, **8**, **11** and dianilides **3**, **6**, **9** and **12**, respectively, were prepared in good yields. One- and two-dimensional ^1H and ^{13}C NMR spectra of prepared compounds have been studied. Chemical shifts of protons could be assigned on the basis of the two-dimensional nuclear Overhauser (NOESY) spectroscopy and homonuclear correlation (COSY) spectra. Chemical shifts of substituted carbons were assigned using two-dimensional $^1H/^{13}C$ heteronuclear correlation (HETCOR) spectra. The substitution effect on the chemical shifts of thiophene analogues are reported, and the coupling constants $^3J_{H,H}$ are determined. The crystal structure of compound **12** was determinated by X-ray analysis.

INTRODUCTION

Continuing our work on the synthesis[1], the photochemical behavior[2-4] and the spectroscopic properties[5] of thiophene compounds, we turned our attention on the synthesis of thienylenediacrylic acids **1**, **4**, 7 and **10**, their acid chlorides **2**, **5**, **8** and **11** and dianilides **3**, **6**, **9** and **12**. Although the thienylenediacrylic acids **1**, **4**, 7 and **10** were prepared earlier[6] we applied a different synthetic pathway using the catalytic Heck vinylation of bromo- or dibromo thiophenes. Palladium catalyzed coupling of bromo- or iodo-substituted aromatic coumpounds with vinyl substituted reagents (ethylacrylate, acylonitrile, styrene, vinymethyl ketone) is a well known and useful reaction for the preparation of vinyl aromatic compounds[7-10]. However, there is not much reported data about the catalytic vinylation of heterocyclic compounds [11,12].

In this paper we report the total assignment of ^1H and ^{13}C NMR spectra of thiophene derivatives **1-12**. The spectra were studied considering the substituent effects. $^3J_{H,H}$ coupling constants were also determined, as the crystal structure of compound **12** by X-ray analysis.

RESULTS AND DISCUSSION

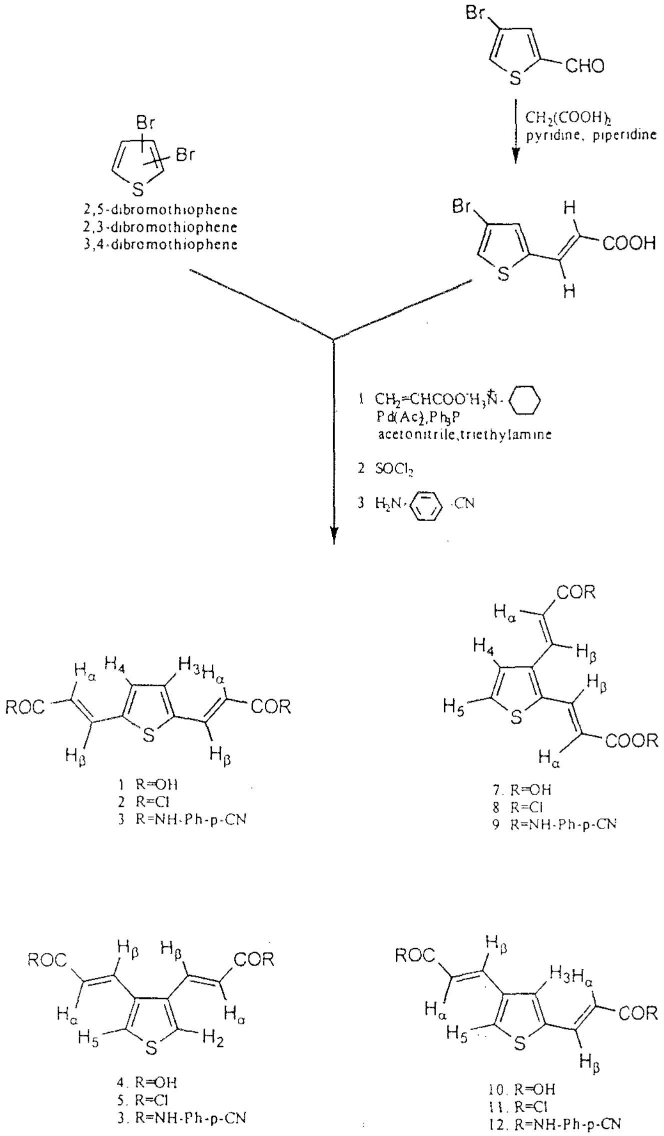
Synthesis

Although 3-(4-bromo-2-thienyl)acrylic acids were prepared earlier by Wittig reaction[13] on the 4-bromo-2-thienylcarboxaldehyde, we prepared this acid by condensation with malonic acid. All diacrylic acids **1**, **4**, **7** and **10** were synthetized by catalytic vinylation of bromo- or dibromo- thiophenes in a one-step reaction according to the Scheme.

The palladium catalyzed vinylation was carried out with the cyclohexylammonium salt of acrylic acid, prepared from cyclohexylamine and acrylic acid. The yields were almost the same as before when we used ethylacrilate[1]. After acidifying the reaction mixture the corresponding acids were isolated in good yields. It could be noticed that yields were better in the case of the divinylation reaction in comparison with the monovinylation reaction. Diacid dichlorides **2**, **5**, **8** and **11** were prepared from acids **1**, **4**, **7** and **10** with excess of $SOCl_2$. Dianilides **3**, **6**, **9** and **12** were prepared from dichlorides **2**, **5**, **8** and **11** and 4-aminobenzonitrile in toluene.

NMR Study

Because of the high degree of molecular symmetry of the thiophene derivatives **1-6**, the carbons are chemically equivalent resulting in a decrease of their NMR signals by half (Table 1 and Table 2). Homo- and hetero-correlated two-dimensional spectra revealed expected cross-peaks, whereas in NOESY spectra except in the cross-peaks of closest neighbors, the cross-peaks between H-2β and H-3, and between H-5β and H-4 in compounds **1-3**, between H-3β and H-2, and between H-4β and H-5 in the compounds **4-6** can be observed, respectively. Except for mentioned cross-peaks, the spectrum of compound **2** revealed correlation between H-2α/H-3, and H-5α/H-4, whereas in compound **4** cross-peaks between H-3α and H-2, and between H-4α and H-5 can be observed. On the other hand the NOESY spectra of compounds **3** and **6** revealed the correlation H-2β/NH and H-5β/NH, and H-3β/NH and H-4β/NH, respectively. Substitution of H-2 and H-5 with vinyl groups in compounds **1-3**, cause downfield shifts of the closest H-3 and H-4 of approx. 0.6 p.p.m., whereas substitution of H-3 and H-4 in compounds **4-6** cause downfield shifts of H-2 and H-5 of approx 0.9 p.p.m., respectively, in comparison with chemical shifts of starting thiophene[14,15] (Table 1). These substitutions cause in carbon spectra the same effects. Carbon pairs in the compounds **1-3**, the C-2 and C-5 are downfield shifted for approx. 16.5 p.p.m., whereas C-3 and C-4 for approx. 6 p.p.m., respectively [16,17]. In the compounds **4-6**, the


Br
CHO
S
CH₂(COOH)₂
pyridine, piperidine
Br
Br
S
2,5-dibromothiophene
2,3-dibromothiophene
3,4-dibromothiophene
Br
H
COOH
S
H
1 CH₂=CHCOO⁻H₃N⁺-
Pd(Ac)₂,Ph₃P
acetonitrile,triethylamine
2 SOCl₂
3 H₂N- -CN
ROC
COR
S
Hα
H4
H3
Hβ
1 R=OH
2 R=Cl
3 R=NH-Ph-p-CN
COR
COOR
H5
7. R=OH
8 R=Cl
9 R=NH-Ph-p-CN
H2
4. R=OH
5. R=Cl
3. R=NH-Ph-p-CN
10. R=OH
11. R=Cl
12. R=NH-Ph-p-CN

SCHEME

Table 1. ^{1}H chemical shifts and ^{3}J coupling constants of thiophene derivatives 1 - 12

Compound	1 (2,5)	2 (2,5)	3 (2,5)	4 (3,4)	5 (3,4)	6 (3,4)	7 (2,3)	8 (2,3)	9 (2,3)	10 (2,4)	11 (2,4)	12 (2,4)
substituent	OH	Cl	NHArCN	OH	Cl	NHArCN	OH	Cl	NHArCN	OH	Cl	NHArCN
H-2	-	-	-	8.163	8.176	8.027	-	-	-	-	-	-
H-3	7.521	7.526	7.534	-	-	-	-	-	-	7.908	7.925	7.776
H-4	7.521	7.526	7.534	-	-	-	7.596	7.614	7.442	-	-	-
H-5	-	-	-	8.163	8.176	8.027	7.718	7.740	7.839	8.047	8.066	8.044
H-2α	7.718	7.720	7.832	-	-	-	7.888	7.894	7.992	7.681	7.680	7.847
H-3α	-	-	-	7.612	7.612	7.709	7.717	7.722	7.792	-	-	-
H-4α	-	-	-	7.612	7.612	7.709	-	-	-	7.532	7.533	7.606
H-5α	7.718	7.720	7.832	-	-	-	-	-	-	-	-	-
H-2β	6.243	6.246	6.639	-	-	-	6.232	6.244	6.682	6.250	6.256	6.632
H-3β	-	-	-	6.408	6.410	6.720	6.497	6.531	6.718	-	-	-
H-4β	-	-	-	6.408	6.410	6.720	-	-	-	6.369	6.372	6.642
H-5β	6.243	6.246	6.639	-	-	-	-	-	-	-	-	-
COOH	12.450	-	-	12.427	-	-	12.501	-	-	12.433	-	-
NH	-	-	10.688	-	-	10.758	-	-	10.723	-	-	10.702 10.723
ArH-2,6	-	-	7.814	-	-	7.797	-	-	7.806	-	-	7.796
ArH-3,5	-	-	7.879	-	-	7.900	-	-	7.871	-	-	7.896
$^{3}J_{H3-H4}$	0	0	0	-	-	-	-	-	-	-	-	-
$^{3}J_{H4-H5}$	-	-	-	-	-	-	5.22	4.88	5.39	-	-	-
$^{3}J_{H2\alpha-H2\beta}$	15.57	15.56	15.57	-	-	-	15.44	15.55	15.17	15.80	15.80	15.33
$^{3}J_{H3\alpha-H3\beta}$	-	-	-	15.84	15.87	15.56	15.72	15.83	15.48	-	-	-
$^{3}J_{H4\alpha-H4\beta}$	-	-	-	15.84	15.87	15.56	-	-	-	15.95	15.94	15.63
$^{3}J_{H5\alpha-H5\beta}$	15.87	15.87	15.87	-	-	-	-	-	-	-	-	-
$^{3}J_{ArH2(6)-ArH3(5)}$	-	-	8.54	-	-	8.54	-	-	8.39	-	-	8.49

Table 2. ^{13}C chemical shifts of furane and thiophene derivatives 1 - 12

Compound	1 (2,5	2 (2,5)	3 (2,5)	4 (3,4)	5 (3,4)	6 (3,4)	7(2,3)	8 (2,3)	9 (2,3)	10(2,4)	11(2,4)	12 (2,4)
substituent	OH	Cl	NHArCN	OH	Cl	NHArCN	OH	Cl	NHArCN	OH	Cl	NHArCN
C-2	141.55	141.54	141.63	127.66	127.70	127.51	139.11	139.04	139.43	140.27	140.20	141.13
C-3	132.87	132.87	133.13	135.53	135.56	136.10	138.51	138.49	138.41	129.59	129.58	129.48
C-4	132.87	132.87	133.13	135.53	135.56	136.10	127.53	127.54	126.85	138.56	138.51	138.63
C-5	141.55	141.54	141.63	127.66	127.70	127.51	129.50	129.52	129.21	132.02	132.05	131.31
C-2a	119.50	119.46	121.90	-	-	-	119.96	119.93	122.36	119.07	119.01	121.54*
C-3a	-	-	-	121.37	121.70	123.69	121.80	121.78	123.96	-	-	-
C-4 a	-	-	-	121.37	121.70	123.69	-	-	-	119.83	119.79	121.92*
C-5a	119.50	119.46	121.90	-	-	-	-	-	-	-	-	-
C-2b	136.39	136.40	134.06	-	-	-	133.37	133.34	130.88	136.52	136.48	134.34
C-3b	-	-	-	135.59	135.65	135.67	134.16	134.11	131.73	-	-	-
C-4b	-	-	-	135.59	135.65	135.67	-	-	-	137.53	137.49	135.06
C-5b	136.39	136.40	134.06	-	-	-	-	-	-	-	-	-
CO	167.31	167.27	163.90	167.73	167.71	164.39	167.32 168.00	167.25 167.93	163.77 164.39	167.49 168.10	167.43 168.03	163.99 164.62
CN	-	-	105.31	-	-	105.32	-	-	105.34	-	-	105.20 105.30
Ar-C-1	-	-	143.57	-	-	143.73	-	-	143.50 143.55	-	-	143.65 143.77
Ar-C-2,6	-	-	133.62	-	-	133.60	-	-	133.50	-	-	133.58 133.63
Ar-C-3,5	-	-	119.50	-	-	119.62	-	-	119.49 119.57	-	-	119.47 119.53
Ar-C-4	-	-	119.29	-	-	119.36	-	-	119.19	-	-	119.36

substitution of C-3 and C-4 shift their signals downfield for approx 9 p.p.m., whereas unsubstituted C-2 and C-5 are shifted downfield for approx. 2.5 p.p.m., respectively [16,17] (T 2).

Coupling constants $^3J_{H\text{-}\alpha,H\text{-}\beta}$ in thiophene series are approx. 15.5 Hz (Table 1) and agree well with the corresponding constants in the substituted vinyl compounds[18]. Coupling constants $^3J_{H\text{-}2(6),H\text{-}3(5)}$ in the benzene nuclei, in the compounds **3**, **6**, **9**, and **12** are approx. 8.5 Hz, and are in good agreement with published data for substituted benzenes[18]. Coupling constants $^3J_{H\text{-}3,H\text{-}4}$ in compounds **1-3** were not observed (J=0), whereas in compounds **7-9** coupling constants $^3J_{H\text{-}4,H\text{-}5}$ were approx. 5 Hz. As a starting point for the assignment of the proton NMR spectra of **7-9**, it is reasonable to expect that the H-4 and H-3β (or H-3α) protons give NOESY cross-peaks (Figure 1) and make it possible to distinguish the H-4 and H-5, and H-2β and H-3β protons, respectively. In NOESY spectra, except the cross-peaks of closest neighbors, the cross-peaks between H-2α and H-3α in compound **7**, and between H-2β and NH in compound **9** can be observed, respectively. A similar type of data give NOESY spectra of compounds **10-12**. H-3 protons have cross-peaks with H-2β and H-4β protons (Figure 2).

On the other hand H-5 protons are correlated with H-4β protons, only. In NOESY spectrum of compound **12** interaction between H-2β and amino group, and H-4 β and amino group were observed. Substitution of C-4 with a vinyl group in compounds **4-6** and **10-12** shifted downfield the H-5 signals for approx. -0.8 p.p.m. The amidation of carboxyl groups in compounds **3**, **6**, **9** and **12** caused similar downfield shift of α vinyl protons (Table 1), and larger effect on β vinyl protons (-0.4 p. p. m.).

In ^{13}C spectra the amidation caused the same effect, but downfield shifts of the α vinyl carbons were larger, approx., -2.5 p.p.m., whereas the β vinyl carbons were shifted upfield approx. 2.5 p.p.m. (Table 2). Substitution of C-2 with a vinyl group caused in ^{13}C spectra the downfield shifts in range 14-16 p.p.m., in the case of C-3 these effects were smaller, between 9 and 12 p.p.m., substitution of C-4 resulted with the downfield shifts in range 9-12 p.p.m, whereas substitution of C-5 caused downfield shift of approx. 16 p.p.m.(Table 2).

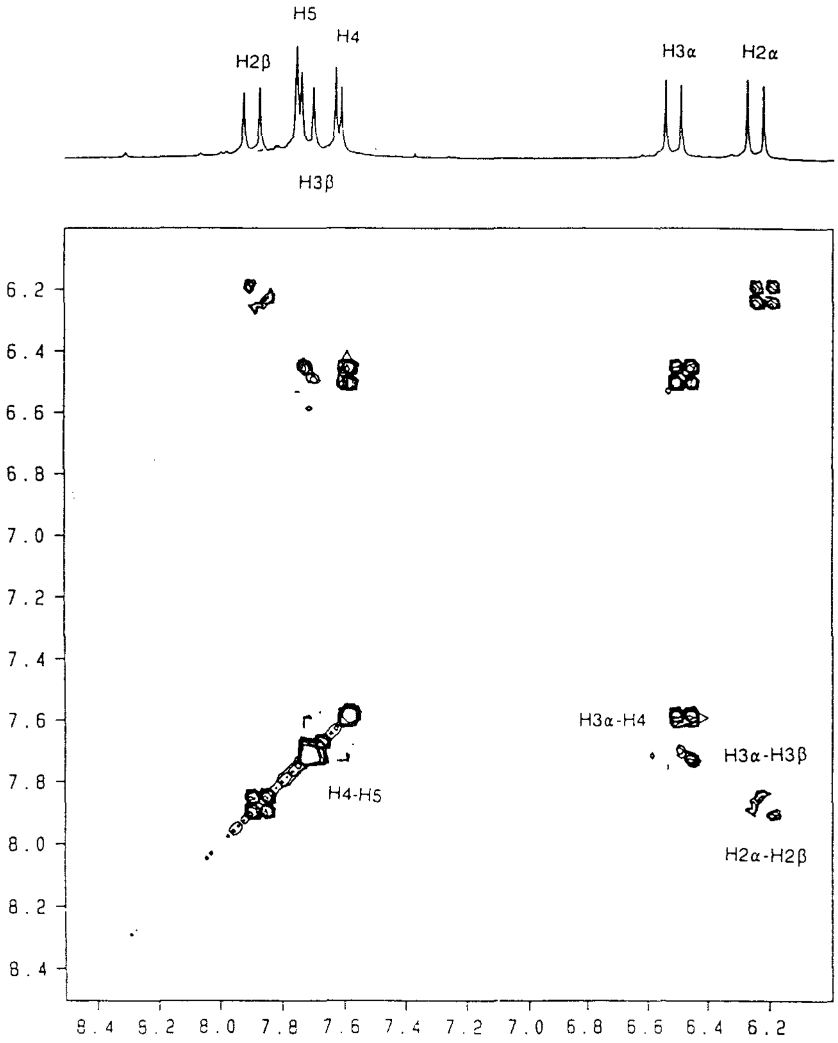


FIG 1: NOESY (phase sensitive mode) spectrum of 2,3-thienylenediacrylic acid dichloride 8 in deuteromethylsulfoxide, 10 mM, 30 °C, mixing time, t_m = 450 ms

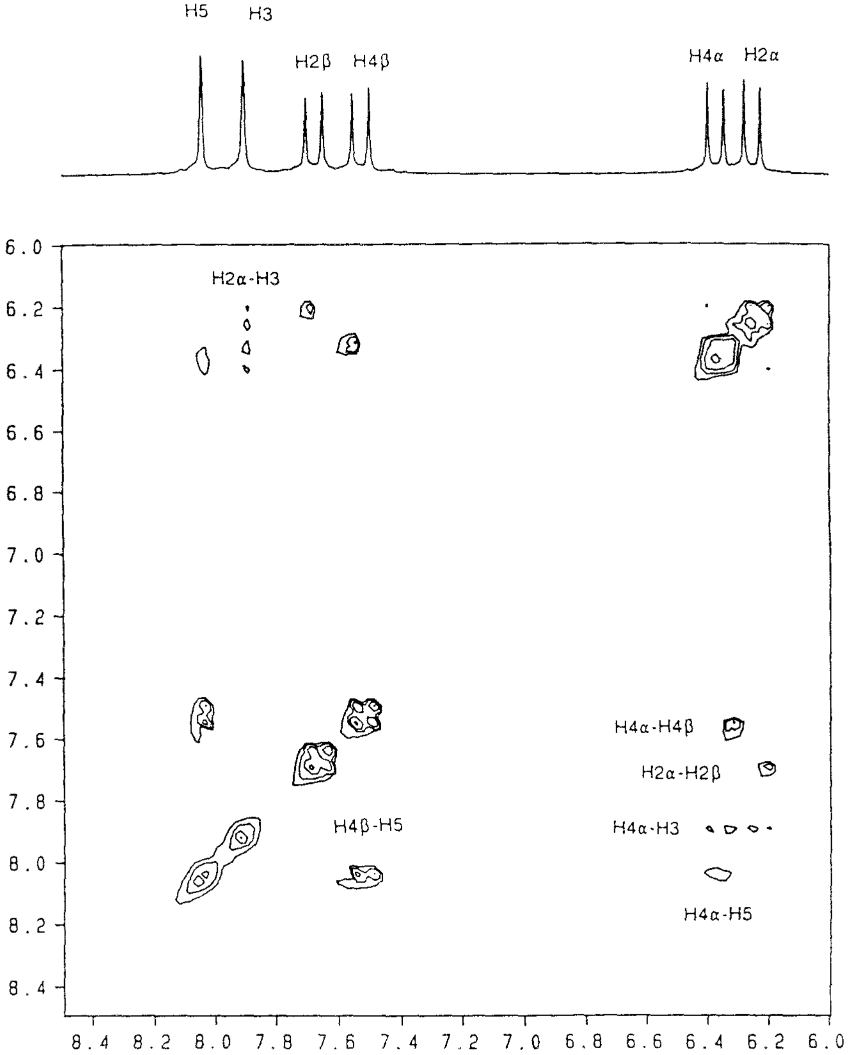


FIG 2: NOESY (phase sensitive mode) spectrum of 2,4-thienylenediacrylic acid 10 in deuteromethylsulfoxide, 10 mM, 30 °C, mixing time, t_m = 450 ms

TABLE 3: Selected bond lengths (A) and angles (°) in the crystal structure of the compound 12

S -C1	1.737(4)	S -C4	1.75(2)
C1 -C2	1.376(4)	C2 -C3	1.396(4)
C3 -C4	1.36(2)	C1 -C15	1.446(4)
C3 -C5	1.454(5)	N2 -C14	1.141(4)
N4 -C24	1.130(4)	C5 -C6	1.316(4)
C15-C16	1.321(4)		
C1-S-C4	90.8(6)	C2-C1-S	110.5(3)
C1-C2-C3	114.4(3)	C4-C3-C2	112.2(8)
C3-C4-S	112(1)		

X-ray Structure Analysis of 12

The molecular structure of **12** is shown in FIGURE 3. The bond lengths and angles are within expected values, except in the region of the thiophene ring, (Table 3, Figure 3).

Although the bond lengths involving the disordered atoms in the thiophene ring have relatively high standard deviations, it is still evident that the bonds in the ring are shorter than the corresponding single bonds and are indicative of π- orbital delocalization over the thiophene ring [19,20,21]. Least-squares planes calculations showed that two planar parts of the molecule are twisting about the axis through the C16 and C17 atoms with an interplanar dihedral angle od 19.5(7)°. In the crystal structure the molecules of **12** are linked by N1-H ... O2 of 3.050(3)A with angles N1-H ... O2 of 153.9(2)° (N1-H 0.844(2) and H ... O2 2.269(2) A).The molecules of **12** are connected to DMF solvent molecules by N3-H ... O3 hydrogen bonds of 2.833(4)A with angles

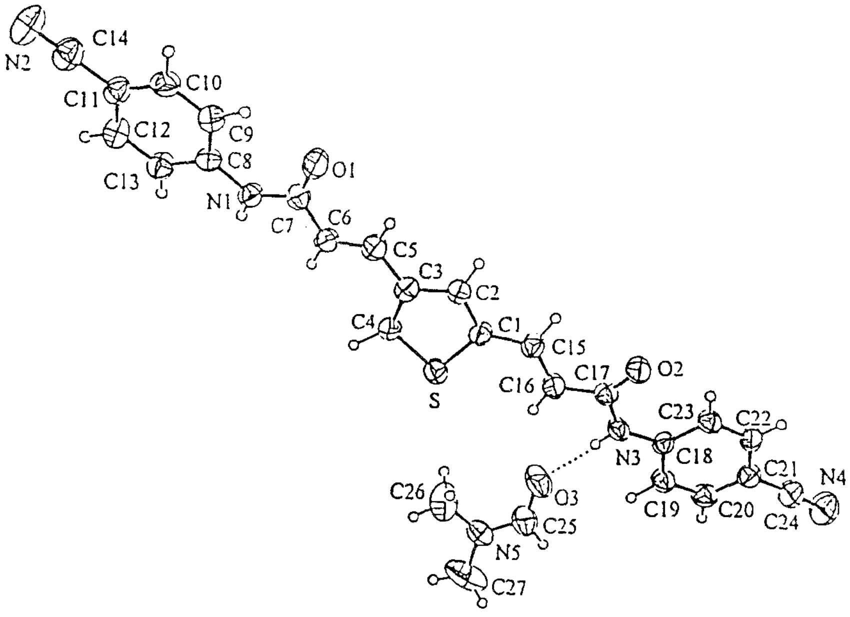


FIG 3: ORTEP view of the bis-anilide 12 with the atom labelling scheme, and the hydrogen-bond motive in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. The disorder in the thiophene ring is not shown and only the atoms with the highest occupancy are given.

N3-H ... O3 171.5(2)° (N3-H 0.821(3) and H ... O3 2.018°) A (Figure 4). Enantiomeric pairs of molecules are stacked along c-axis with only van der Waals contacts between them.

EXPERIMENTAL

Melting points were obtained with a Kofler block and are uncorrected. IR spectra were taken using a Perkin-Elmer 257 spectrophotometer in KBr pellets.

Preparation of 3-(4-bromo-2-thienyl)acrylic acids

3-(4-Bromo-2-thienyl)acrylic acids were prepared by the condensation of 4-bromo-2-thienylcarboxaldehyde (12 g, 0.063 mola) and malonic acid (6,24 g, 0.06

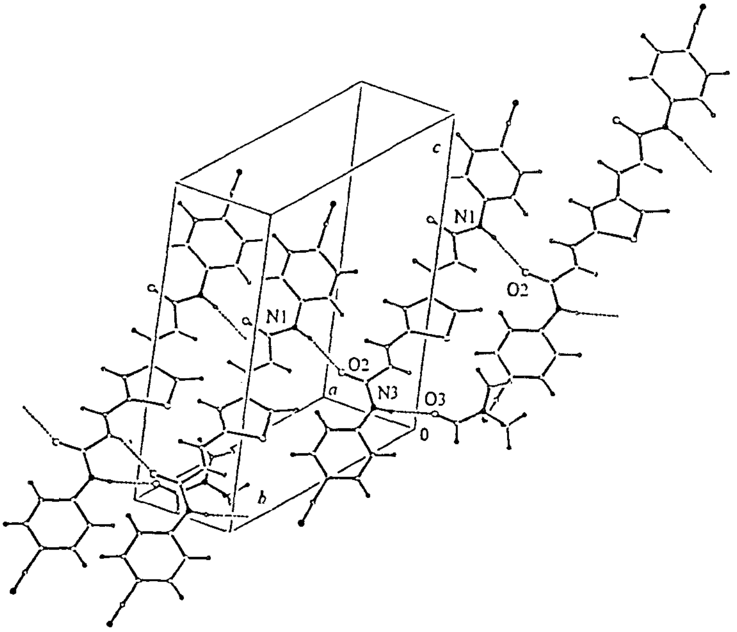


FIG 4: Packing of molecules 12 and solvent (DMF) in the unit cell. Hydrogen bonds are shown by dashed lines.

mola) in the presence of pyridine (48 ml) and piperidine (0.5 ml). Reaction mixture was refluxed 18 hours. After cooling, the contents were poured on ice and acidified with 1N HCl. The crude product was recrystallized from ethanol/water (2.5:1). Yellow crystals 11.83 g (80.85%), mp 141-145 °C were obtained (lit. mp 143-145°C)[13].

Preparation of thienylenediacrylic acids 1,4,7 and 10: General procedure

The mixture of bromo (or dibromo-) thiophenes, cyclohexylammonium salt of acrylic acids, a catalytic amount of palladium acetate and triphenylphospine in acetonitrile and triethylamine was silled in the glass tube and heated 20 hours at 100°C. The reaction mixture was cooled, the solvent evaporated under vacuum, the residue dissolved in water, heated with charcoal, filtered and acidified with 1N HCl. The precipitate was then recrystallized from acetic acid[1]

TABLE 4: Thienylenediacrylic acids 1,4,7 and 10

Comp	Bromo derivate g (mmol)	cyclo-hexyl-amine salt g(mmol)	Aceto nitrile ml	Tri-ethyl-amine ml	Pd(OAc)$_2$ mg	PPh$_3$ mg	Yield g(%)	Mp °C
1	2,5dibromo-thiophene 6.0 (20)	47.67 (280)	154	77	231	180	1.07 (23.3)	285-287
4	3,4dibromo-thiophene 5.0 (20)	39.72 (230)	130	65	193	645	3.08 (66.5)	> 290
7	2,3dibromo-thiophene 5.0 (20)	39.73 (230)	130	65	193	645	3.00 (64.6)	205-210
10	3-(4-bromo-2-thienyl) acrylic acid 2.7 (10)	10.74 (60)	36	18	54	180	1.14 (43.5)	232-235

Preparation of acid chlorides 2, 5, 8 and 11 derived from thienylenediacrylic acids: General procedure

The title compounds were prepared from **1**, **4**, **7** and **10** and an excess of $SOCl_2$ by refluxing the reaction mixture for 4 hours. The excess of $SOCl_2$ was distilled off under vacuum, and the residue crystallized from benzene and cyclohexane (1:1).

Preparation of dianilides 3, 6, 9 and 12 derived from thienylenediacrylic acids: General procedure

The new title compounds were prepared from corresponding dichlorides **2**, **5**, **8** and **11**. The solution of p-aminobenzonitrile in toluene was dropped into the solution of diacid dichloride in toluene by stirring at room temperature. The reaction mixture was refluxed for 1 hour. After cooling, the crystals were filtered off, washed with water and recrystallized from DMF:water (3:1).

NMR Techniques

The one- and two-dimensional NMR spectra were recorded at room temperature or at 30°C with a Varian Gemini 300 spectrometer operating at 300.1 (^1H) and 75.0 (^{13}C)

TABLE 5: Thienylenediacrylic acids dichlorides 2, 5, 8 and 11

Comp.	Diacrylic acid g (mmol)	$SOCl_2$ ml(mmol)	Yield g(%)	Mp °C	Elemental analysis Calcd.(%)Found(%)
2	1 0.84 (4)	3.2 (40)	0.262 (25.4)	232- 235	C 45.99 46.04 H 2.32 2.20
5	4 3.15 (10)	16.38 (230)	0.60 (16.2)	145-149	C 45.99 45.78 H 2.32 2.17
8	7 2.69 (10)	14.0 (190)	0.61 (21.0)	116-119	C 45.99 46.03 H 2.32 2.15
11	10 0.60 (3)	31.5 (430)	0.32 (46.1)	121-125	C 45.99 46.12 H 2.32 2.08

TABLE 6: Thienylenediacrylic acids dianilides 3, 6, 9 and 12

Comp.	Acid's dichloride g (mmol)	4-Amino-benzo-nitrile g (mmol)	Solvent (toluene) ml	Yield g(%)	Mp °C	Elemental analysis Calcd.(%)Found(%)
3	2 0.262(1.0)	0.35 (30)	160	0.106 (26.9)	> 300	C 63.82 63.72 H 4.28 4.04
6	5 0.58 (2.0)	0.78 (10)	28	0.79 (90.8)	> 300	C 63.82 63.86 H 4.28 4.31
9	8 0.051(2.0)	0.70 (10)	25	0.75 (71.5)	267-270	C 63.82 63.90 H 4.28 4.39
12	11 0.32 (1.0)	0.44 (1.0)	19	0.32 (66.0)	284-288	C 63.82 63.77 H 4.28 4.57

MHz, respectively. Typically, each one-dimensional ^1H NMR spectrum was collected using a single 30° (6 μs) pulse, 1s relaxation delay time, with the aquisition time 1.9 s, and a total sweep width of 5000 Hz sampled with 32 k points. Data processing employed a Lorentz linebroadening factor of 0.5 Hz. Using these conditions, the experimental error of the measured coupling constants were ±0.31 Hz. One-dimensional ^{13}C NMR spectra were acquired using a single 45° (6 μs) pulse, 0.6 relaxation delay time, aquisition time 0.7 s, and a total sweep width of 19000 Hz sampled with 32 k points. Data processing employed a Lorentz linebroadening factor of 1.2 Hz. The spectra were referenced to the residual DMSO signal (2.51 or 39.6 p.p.m., respectively). Concentrations of samples used for ^1H spectra were approx. 10 mM, and 100 mM for ^{13}C NMR spectra.

Two-dimensional experiments: COSY[22,23], NOESY[24-26] and HETCOR[27,28] were performed using standard pulse sequences of the Varian Gemini software package. The COSY spectra were obtained in the magnitude mode, whereas NOESY spectra were obtained in the phase-sensitive mode[29]. The COSY and NOESY experiments had 1024 points in the F2 dimension and 256 slices in F1, which were zero-filled to 1024 points. Each slice was obtained using 16 scans, a relaxation delay of 1 s, and a spectral width of 4200 Hz. The resolution in both domains was 8.4 Hz/point. The NOESY employed a mixing time of 450 ms. The samples for NOESY spectra were degassed and NMR tubes were filled with argon.

The HETCOR experiment had 2048 points in F2 dimension and 512 slices in F1, which were zero-filled to 1024 points. Each slice was obtained using 128 scans, a relaxation delay of 1 s, and the spectral width was 19000 Hz in F2, and 4500 Hz in F1 domains, respectively. The resolution in F2 was 18.6 Hz/point, and 8.8 Hz/point in F1 dimension. The protons were decoupled with Waltz-16 modulation.

X-ray Structure determination of 2,4-thienylenediacrylic acid dianilide 12

The pale-yellow crystals, were grown by slow evaporation of a dilute solution of acetone/DMF mixture (1:1). Crystal data: $C_{24}H_{16}N_4O_2S$ x C_3H_7NO

Mr = 497.56
Triclinic
P -1 (No. =2)
a = 8.172(2) A
b = 12.242(2) A
c = 14.038(3) A
α = 111.08 (1)°
β = 90.20(2)°
γ=103.58(2)°
V= 1267.8(5) A^3
Z = 2

Mo K_α radiation
λ = 0.71073 A
Cell parameters from 35 reflections
Θ = 9.2 - 12.5°
μ = 1.66 cm^{-1}
T = 295(1)K
Dx = 1.303 Mg m^{-3}
Dm = not measured

A regular crystal with dimensions 0.15 x 0.19 x 0.65 mm was used for intensity data collection by the Θ-2Θ scan technique in range of 2.58-<Θ-<27.0°,(h = - 10→10, k = - 15→ 14, l = - O→17). Four check reflections monitored every two hours showed no significant crystal decomposition (2.8%). The data were corrected for the Lorentz and polarization factors but not for absorption. Further calculations used 5507 unique reflections, of which 2266 were with $F^2>\sigma(F^2)$. All non-H atoms in the structure were found by direct methods. A positional disorder of the S and C atoms in the thiophene ring was found. The refinement showed in one case (S and C4) the occupation factor amounted to 0.582(5), and in the other case (S′ and C4′) 0.418(5). The C3-S′, S′-C4′ and C4′-C1 bond lengths involving atoms with the smaller occupancy were restrained to be equal to the corresponding distances involving atoms with higher occupancy. The temperature factors of the S and C4′ and C4 and S′ pairs were constrained to be equal. Hydrogen atoms were located either in a difference Fourier map or generated from the assumed geometries for the methyl groups C26, C27 of the solvent molecule. Full-matrix least-squares refinement of 405 parameters, on F^2 converged $((\text{shift/e.s.d.})_{\text{mean}} = 0.02)$ at R = 0.059 and wR =0.121 (for $F^2>2\sigma(F^2)$), S = 0.987, $w = 1/[\sigma^2(F_o^2) + (0.0756P)^2 + 0.1727P]$ where $P = (F_o2 + 2F_c^2)/3$. Final Δρ values were -0.18 to + 0.19 eA^{-3}. The final atomic coordinates with equivalent isotropic thermal parameters are given in Table 7. The observed and calculated structure factors are obtained from the authors on request. All calculations were performed on an IBM PC/AT compatible

TABLE 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (x 10^3 Å^2) fornon-H atoms of the compound 12

	x	*y*	*z*	U_{eq}[a]
S[b]	1351(3)	444(2)	7080(3)	67(1)
C4'[b]	964(21)	120(13)	6962(17)	67(1)
N1	-2580(3)	3678(3)	4965(2)	56(1)
N2	-5490(5)	6603(3)	2320(3)	107(1)
N3	1443(3)	-3339(3)	8105(2)	54(1)
N4	2164(5)	-7246(3)	10360(3)	114(1)
N5	6606(3)	132(3)	8819(2)	76(1)
O1	-4212(3)	1750(2)	4323(2)	86(1)
O2	-867(3)	-4240(2)	6930(2)	68(1)
O3	4171(4)	-1239(2)	8703(2)	96(1)
C1	-425(4)	-770(3)	6652(2)	56(1)
C2	-1646(4)	-502(3)	6161(3)	59(1)
C3	-1179(4)	643(3)	6102(3)	60(1)
C4[b]	372(18)	1290(17)	6601(20)	64(1)
S'[b]	813(5)	1333(6)	6626(7)	64(1)
C5	-2213(5)	1117(3)	5581(3)	63(1)
C6	-1928(4)	2211(3)	5560(3)	61(1)
C7	-3022(4)	2506(3)	4904(3)	59(1)
C8	-3241(4)	4214(3)	4377(2)	51(1)
C9	-4502(4)	3590(3)	3568(3)	60(1)
C10	-5080(4)	4201(3)	3033(3)	63(1)
C11	-4415(4)	5431(3)	3291(3)	60(1)
C12	-3143(5)	6048(4)	4093(3)	67(1)
C13	-2563(4)	5441(3)	4616(3)	62(1)
C14	-5028(5)	6074(4)	2742(3)	78(1)
C15	-580(4)	-1890(3)	6816(3)	58(1)
C16	594(4)	-2199(3)	7239(3)	60(1)
C17	301(4)	-3353(3)	7388(2)	53(1)
C18	1502(4)	-4207(3)	8524(2)	48(1)
C19	2866(4)	-3928(3)	9245(3)	58(1)
C20	3002(4)	-4702(3)	9721(3)	64(1)
C21	1801(4)	-5795(3)	9479(3)	59(1)
C22	453(4)	-6068(3)	8769(3)	59(1)
C23	274(4)	-5293(3)	8296(3)	56(1)
C24	1986(4)	-6611(4)	9974(3)	79(1)
C25	5695(6)	-836(4)	8962(3)	81(1)
C26	5836(6)	767(4)	8329(4)	112(2)
C27	8346(5)	623(5)	9244(4)	132(2)

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[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Disordered atoms with the following site occupation factors (%) : S, C4 58.2(5) ; S', C4' 41.8(5).

microcomputer using SHELXS-86[30], SHELXL-93[31], ORTEP[32] and PLUTON-93(33) programs.

Crystallographic data for the structure reported in this paper have been deposited at Cambridge Cryatallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: + 44-1223-336003; e-mail deposit cccdc.cam.ac.uk.) and can be obtained on request, free of charge, by quoting the publication citation and the deposition number 100484.

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