Rotational Isomerism in the Radical Anions of Bi- and Ter-aryls containing the Thiophen Ring

By **Gian Franco Pedulli,*** Istituto Chimico dell'Università, Via Ospedale 72, 09100 Cagliari, Italy
Marcello Tiecco, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Perugia, Perugia, Italy
Maurizio Guerra and **Giorgio Martelli,** Laboratorio dei composti del carbonio contenenti eteroatomi e loro applicazioni del C.N.R., Via Tolara di Sotto 89, Ozzano Emilia (Bologna), Italy
Paolo Zanirato, Istituto di Chimica Organica, Viale Risorgimento 4, 40136 Bologna, Italy

The conformational behaviour of the radical anions of several bi- and ter-aryls has been investigated by e.s.r. spectroscopy. Comparison with their diamagnetic precursors shows that the addition of the unpaired electron to the π-system greatly increases the conformational rigidity of these compounds. This result is accounted for by INDO MO calculations, and can be rationalized in terms of the occupancy by the unpaired electron of the lowest vacant orbital of neutral bi- and ter-aryls which has a strong bonding character in the interannular regions.

THE conformational properties of organic radicals may be conveniently investigated by means of e.s.r. spectroscopy since the intrinsic time scale of this technique is short enough to allow the detection of isomers having lifetimes of only 10^{-5} s or even less. The radical anions of aromatic derivatives are particularly interesting substrates in this respect, since the addition of the unpaired electron to the unsaturated system is expected to produce substantial modifications of the electronic structure of the diamagnetic precursors. This may affect both the isomer stability and the height of the energy barrier to conformational interconversion; examples of this behaviour have been described in the case of aromatic ketyls and bridged diphenyls.[1-3]

---

[1] M. Guerra, G. F. Pedulli, M. Tiecco, and G. Martelli, *J.C.S. Perkin II*, 1974, 562; F. Bernardi, M. Guerra, and G. F. Pedulli, *J. Phys. Chem.*, 1974, **78**, 2144.

[2] G. F. Pedulli, A. Alberti, M. Guerra, G. Seconi, and P. Vivarelli, *J.C.S. Perkin II*, 1976, 173.

[3] G. F. Pedulli, P. Zanirato, A. Alberti, and M. Tiecco, *J.C.S. Perkin II*, 1975, 293.

We report here an investigation on several radical anions of bi- and ter-aryls containing the thiophen ring with the aim of clarifying their conformational behaviour with respect to the corresponding neutral molecular species and the factors influencing the energy barriers to isomer interconversion.

We chose substituted thiophens since they have proved to be useful and versatile compounds for this kind of study because of the long lifetime of the corresponding radicals, the lower symmetry of thiophen with respect to other aromatic rings, and the reduced number of nuclei interacting with the unpaired electron. A number of experimental and theoretical investigations have appeared concerning rotational isomerism in thiophen-containing radicals such as mono-[1,4] and diketyls,[5] monoaryl nitroxides,[6] trithienylmethyls,[7] and 1,2-dithienylethylenes.[8]

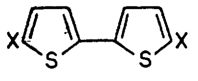
Preliminary results have also been reported by us for the radical anions of 2-2′-bithienyl and 2-phenylthiophen,[9] the first examples of detection by e.s.r. spectroscopy of restricted rotation in thiophen radicals.

EXPERIMENTAL

2,2′-Bithienyl [10] (Ia), 2,2′-bithienyl-5-5′-dicarbaldehyde [11] (Ic), 2,2′-dinitro-5,5′-bithienyl [12] (Id), 5,5′-dideuterio-2,2′-bithienyl [9] (Ie), 3,3′-bithienyl [13] (II), 2,3′-bithienyl [14] (III), 2-phenylthiophen [15] (IV), 4-(2-thienyl)pyridine [16] (V), 4-phenylpyridine [16] (VI), 2,5-diphenylthiophen [17] (VII), and *p*-di-(2-thienyl)benzene [18] (VIIIa) were prepared as described in the literature.

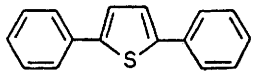
5,5′-Dicyano-2,2′-bithienyl(Ib).—A solution of 2-bromo-5-cyanothiophen (1 g) in dimethylformamide (30 ml) was refluxed 3 h in the presence of copper bronze (0.2 g). The mixture was poured onto dilute hydrochloric acid and extracted into chloroform. The organic layer was washed with water, dried, and evaporated. The solid *residue* was crystallized by chloroform and light petroleum (b.p. 40—60°), m.p. 256—258° (Found: C, 55.2; H, 1.95; N, 13.05; S, 30.0. $C_{10}H_4N_2S_2$ requires C, 55.5; H, 1.85; N, 12.95; S, 29.65%).

Dithieno[3,2-b;2′,3′-d]*thiophen*-2,6-*dicarbaldehyde* (IX).—To a solution of dithieno[2,3-*b*;2′,3′-*d*]thiophen [19] (1.5 g) in acetic acid (80 ml), *N*-bromosuccinimide (2.9 g) was added in portions. The mixture was stirred for 2 h, poured into water, and extracted with chloroform; the organic layer was washed with dilute sodium hydrogen carbonate solution, and with water. The solvent was evaporated and the residue was crystallized from light petroleum (b.p. 100—120°). 2,6-*Dibromodithieno*[3,2-b;-2′,3′-d]*thiophen* (2.7 g) was obtained as a solid, m.p. 166—168° (Found: C, 27.4; H, 0.6; Br, 45.0; S, 27.4. $C_8H_2Br_2S_3$ requires C, 27.15; H, 0.6; Br, 45.15; S, 27.2%). The dibromo-derivative (1 g) was added to a solution of n-butyl-lithium in ether (from 0.2 g of lithium), cooled at −30°. The solution was stirred at −30° for 1 h and dimethylformamide (1 g) in ether (15 ml) was added dropwise. Stirring was continued for 2 h at the same temperature; the mixture was left to reach room temperature and then poured into dilute hydrochloric acid. Excess of chloroform was added and the organic layer was washed with a solution of sodium hydrogen carbonate and with water. The solvent was evaporated and the residue was chromatographed through a silica gel column, using light petroleum (b.p. 40—60°)-acetone (4 : 1) as eluant. After some fractions contained unidentified byproducts, the desired *dialdehyde* was collected (0.4 g), m.p. 273—275° (Found: C, 47.5; H, 1.6; S, 37.95. $C_{10}H_4O_2S_3$ requires C, 47.6; H, 1.6; S, 38.1%).

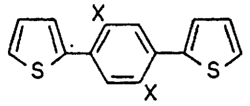


(I)

a ; X = H
b ; X = CN
c ; X = CHO
d ; X = NO2
e ; X = D

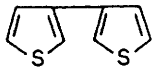


(VII)

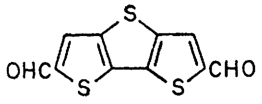


(VIII)

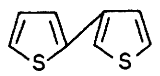
a ; X = H
b ; X = Me



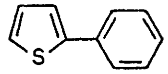
(II)



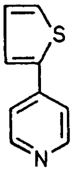
(IX)



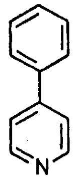
(III)



(IV)



(V)



(VI)

---

[4] A. Hudson and J. W. E. Lewis, *Tetrahedron*, 1970, **26**, 4413.

[5] L. Lunazzi, G. F. Pedulli, M. Tiecco, C. Vincenzi, and C. A. Veracini, *J.C.S. Perkin II*, 1972, 751.

[6] M. Camaggi, L. Lunazzi, G. F. Pedulli, G. Placucci, and M. Tiecco, *J.C.S. Perkin II*, 1974, 1226.

[7] A. Mangini, G. F. Pedulli, and M. Tiecco, *Tetrahedron Letters*, 1968, 4941; F. Bernardi, M. Guerra, G. F. Pedulli, and K. Mislow, *Tetrahedron*, 1976, **32**, 951.

[8] L. Lunazzi, A. Mangini, G. Placucci, P. Spagnolo, and M. Tiecco, *J.C.S. Perkin II*, 1972, 192.

[9] P. Cavalieri d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Letters*, 1969, 4179.

[10] H. Wjnberg and A. Logothesis, *J. Amer. Chem. Soc.*, 1956, **78**, 1958.

[11] R. F. Curtis and G. T. Phillips, *Tetrahedron*, 1967, **23**, 4419.

[12] C. Carpanelli and G. Leandri, *Ann. Chim.* (*Italy*), 1961, **51**, 181.

[13] S. Gronowitz and H. O. Karlsson, *Arkiv Chemi*, 1960, **17**, 89.

[14] H. Wjnberg, A. Logothesis, and D. Ver Ploeg, *J. Amer. Chem. Soc.*, 1957, **79**, 1972.

[15] C. M. Camaggi, G. De Luca, and A. Tundo, *J.C.S. Perkin II*, 1972, 412.

[16] H. Wjnberg, J. J. Van Berger, and R. M. Kellog, *J. Org. Chem.*, 1969, **34**, 3175.

[17] H. Bohme, H. Pfeifer, and E. Schneider, *Ber.*, 1942, **B75**, 900.

[18] P. Ribereau and P. Pastour, *Bull. Soc. chim. France*, 1969, 2076.

[19] F. De Jong and M. J. Janssen, *J. Org. Chem.*, 1971, **36**, 1645.

2,5-*Di*-(2-*thienyl*)-p-*xylene* (VIIIb).—To a solution of the diazonium salt of 2,5-dimethyl-4-nitroaniline[20] (18.5 g) excess of thiophen (200 ml) was added and the mixture was vigorously stirred at 5 °C. A solution of 5M-sodium hydroxide (140 ml) was added dropwise and stirring was continued for 20 h. Ether was added, the organic layer was washed with water, and the solvent evaporated. Column chromatography of the residue, on silica gel, using light petroleum (b.p. 40—60°)-ethyl ether (95 : 5) as eluant, afforded 2-(2,5-*dimethyl*-4-*nitrophenyl*)*thiophen* (4.5 g), m.p. 60—62° (Found: C, 61.75; H, 4.7; N, 6.2; S, 13.55. $C_{12}H_{11}NO_2S$ requires C, 61.8; H, 4.75; N, 6.0; S, 13.75%). Catalytic reduction of this compound (3 g) afforded 2-(4-*amino*-2,5-*dimethylphenyl*)*thiophen* (2 g), b.p. 125—128° at 0.2 mmHg (Found: C, 70.75; H, 6.5; N, 6.75; S, 15.55. $C_{12}H_{13}NS$ requires C, 70.9; H, 6.45; N, 6.9; S, 15.75%). The amine (2 g) was diazotized and treated with thiophen and sodium hydroxide as described above. 2,5-*Di*-(2-*thienyl*)-p-*xylene* (VIIIb) (0.6 g), m.p. 100—101°, was obtained after column chromatography on silica gel, using light petroleum (b.p. 40—60°) as eluant (Found: C, 71.15; H, 5.2; S, 23.5. $C_{16}H_{14}S_2$ requires C, 71.1; H, 5.2; S, 23.7%).

TABLE 1

Hyperfine splitting constants of the radical anions of substituted dithienyls and differences $\Delta B_0 = B_0(trans) - B_0(cis)$ of the resonance fields of the spectral centres of the two isomers

Compound	Solvent	Relative concentration (%)	a_3/G	a_4/G	a_5/G	ΔB_0
(Ia) *trans*	DME	78	4.01	0.75	4.76	0.27
(Ia) *cis*		22	3.97	0.70	4.80	
(Ib) *trans*	DME–THF	55	2.38	0.15	0.99(N)	−0.02
(Ib) *cis*		45	2.50	0.04 *	0.97(N)	
(Ic) *trans*	DMSO	62	0.87	1.36	2.65(CHO)	−0.085
(Ic) *cis*		38	0.66	1.42	2.64(CHO)	
(Id) *trans*	DMSO	66	0.49	1.34	1.65(N)	−0.02
(Id) *cis*		34	0.51	1.15	1.75(N)	
(IX)	DMSO			1.71	2.92(CHO)	

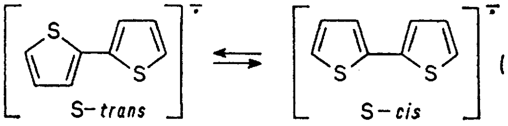
* Determined from computer simulation.

The radical anions were generated by reduction with potassium in degassed dimethoxyethane (DME) or with a sodium–potassium alloy in a 1 : 2 mixture of DME and tetrahydrofuran (THF). In the case of 4-(2-thienyl)-pyridine (V) and 4-phenylpyridine (VI) hexamethylphosphoric triamide (HMPA) was used as solvent. The radicals from the diformyl (Ic) and (IX), and dinitro (Id) derivatives were also produced by treatment with potassium t-butoxide in dimethyl sulphoxide (DMSO) solution. Under these conditions e.s.r. spectra showing better resolution could be obtained, because of the absence of hyperfine splitting from the metal counterion.

INDO Calculations have been carried out on the radical from (Ia), (Ic), (VII), and (VIIIa), by employing a program parametrized for second row elements according to Benson and Hudson.[21] The geometrical parameters for the thiophen ring were kept fixed to values reported for 2,2′-bithienyl,[22] while for phenyl regular hexagonal geometry with a C–C bond distance of 1.39 Å has been assumed.

RESULTS AND DISCUSSION

2,2′-*Bithienyls*.—The e.s.r. spectrum of the radical anion of 2,2′-bithienyl (Ia) generated at −80° in DME shows, as previously reported,[9] the presence of two species with relative concentrations of 4 : 1, characterized by similar hyperfine splittings, which have been identified as the two rotational isomers of this radical.



(Ia)

Since in the neutral 2,2′-bithienyl the *S-trans* isomer is the only observable species in the solid state,[23] and is predominant in liquid crystalline mesophases,[24] we may reasonably assume that the same conformation is also preferred in the corresponding radical anion. This attribution is supported by INDO calculations (see later). The hyperfine splittings reported in Table 1 have been assigned by comparison with the spectrum of 5,5′-dideuterio-2,2′-bithienyl (Ie).

In the hope of measuring the energy barrier to internal rotation, the temperature of the sample was increased with the expectation of observing exchange broadening. Unfortunately no line shape variations could be detected up to −40°, and at higher temperatures the radical rapidly decays. To overcome this difficulty, substituted bithienyls were prepared by introducing at the 5- and 5′-positions stabilizing functions such as cyano, formyl, and nitro. The corresponding radicals were much more stable and spectra could be recorded at higher temperatures. In every case both rotational isomers were detected, as shown in Figure 1, which shows as a representative example the experimental and simulated spectra of the anion radical from the bithienyldicarbaldehyde (Ic). Since in this particular case conformers could also arise from restricted rotation of the formyl groups, we examined the dithienothiophendicarbaldehyde (IX) in which only this kind of isomerism can arise. The e.s.r. spectrum reported in Figure 1c shows the existence of only one isomer which, by analogy with the attribution made for several related

---

[20] E. Nolting, O. N. Witt, and S. Forel, *Ber.*, 1885, **18**, 2664.

[21] H. G. Benson and A. Hudson, *Theor. Chim. Acta.*, 1971, **23**, 259.

[22] A. Almenningen, O. Bastiansen, and P. Svendas, *Acta Chem. Scand.*, 1958, **12**, 1671.

[23] G. J. Visser, G. J. Heeres, J. Wolters, and A. C. Vos, *Acta Cryst.*, 1968, **24B**, 467.

[24] P. Bucci, M. Longeri, C. A. Veracini, and L. Lunazzi, *J. Amer. Chem. Soc.*, 1974, **96** 1305.

dialdehydes,[5] should be that with the formyl oxygens *cis* to the adjacent sulphur atoms. Closer examination of this spectrum reveals the presence at lower field of some lines, weak signals which are certainly due to the *cis–trans*-isomer whose relative amount however does not exceed 5%. We may therefore be sure that in the radical anion of the bithienyldialdehyde (Ic), as in the case of the dicyano (Ib) and dinitro (Id) derivatives, the isomers detected arise from restricted rotation around the inter-annular bond. The measured hyperfine splittings and the relative isomer concentrations are reported in Table 1. The more stable isomer was always assumed to be S-*trans*. The assignment of the coupling constants to the various positions was made for (Ic) by comparison with the e.s.r. spectrum of (IX) and for (Ib) and (Id) by analogy with the radical anions of 4,4′-dicyano-[25] and 4,4′-dinitro-biphenyl.[26]

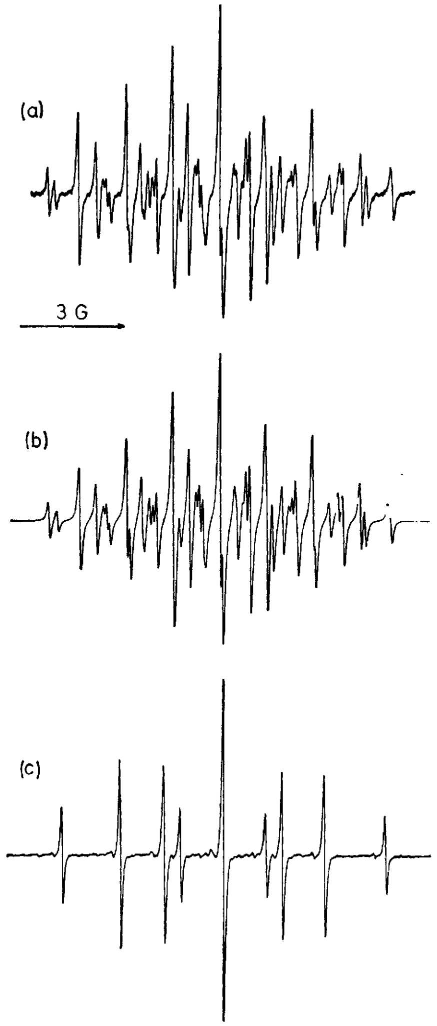


FIGURE 1 Experimental (a) and simulated (b) room temperature e.s.r. spectra of the radical anions of 2,2′-bithienyl-5,5′-dicarbaldehyde (Ic), and (c) of dithieno[3,2-*b*: 2′,3′-*d*]-thiophen-2,6-dicarbaldehyde (IX)

In no case could exchange broadening be observed even at temperatures as high as 100 °C. This indicated that the isomerization process in the negatively charged 2,2′-bithienyl is characterized by a high activation energy; its lower limit can be estimated to be *ca.* 15 kcal mol^{-1}, if the presence of the substituents does not have much effect on the height of the barrier. These findings contrast with the behaviour of neutral 2,2′-bithienyl, where the barrier to S-*cis* $\rightleftarrows$ S-*trans* interconversion has been calculated to be only 4 kcal mol^{-1}.[27] An experimental value of 5 ± 2 kcal mol^{-1} has also been reported from a liquid crystal n.m.r. study of the same compound.[24] An increase in the rotational barrier on going from a neutral derivative to the corresponding radical anion is not unusual; [1] however it is the extent of the increase which is perhaps unexpected.

To clarify this point, INDO MO calculations were employed to compute the potential energy curve of negatively charged 2,2′-bithienyl as a function of the dihedral angle θ between the two rings. The INDO method is suitable for this purpose, since it has been already found to predict successfully the magnitude of rotational barriers in flexible radicals.[1,2,7] Computations were done by keeping fixed the geometry of the

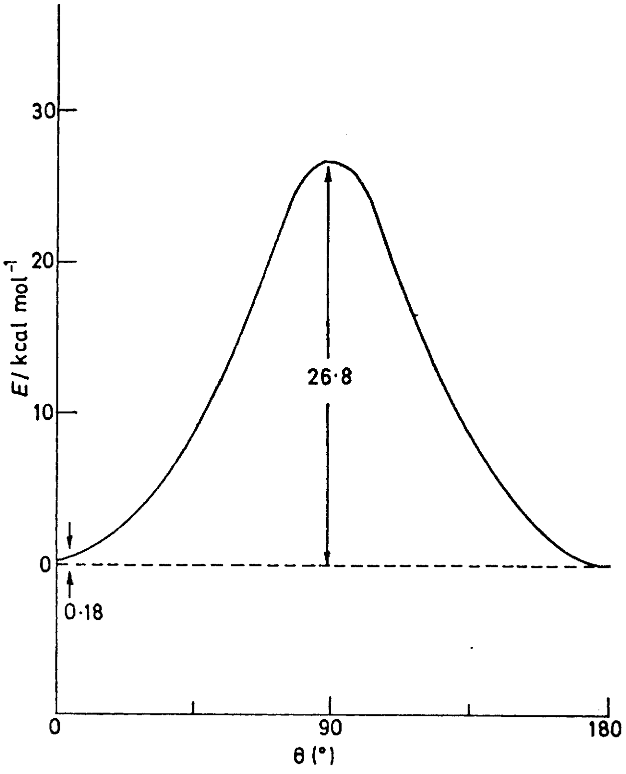


FIGURE 2 INDO potential energy curve for the radical anion of 2,2′-bithienyl as function of the dihedral angle θ between the two rings. The S-*cis* and S-*trans* conformations correspond to θ and 180°, respectively

---

[25] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1963, **85**, 683.

[26] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609.

[27] M. J. S. Dewar and N. Trinajistic, *J. Amer. Chem. Soc.*, 1970, **92**, 1453; V. Galasso and N. Trinajistic, *Tetrahedron*, 1972, **28**, 4419.

thiophen rings, while the interannular bond distance was optimized for each value of θ. The calculated energy curve (Figure 2) shows the S-*trans* conformation to be more stable than the S-*cis* by 0.18 kcal mol^{-1}, in reasonable agreement with experiment. The energy barrier to rotation is 26.8 kcal mol^{-1}. Such a large value which accounts for the observed absence of line broadening in the e.s.r. spectra of the radical anions of 2,2'-bithienyls, depends on occupation by the unpaired electron of the LUMO of 2,2'-bithienyl giving a strong bonding character to the C(2)–C(2') link. Conjugation of the two rings will therefore be favoured in the radical and the energy difference between the planar and the perpendicular conformations is much greater than in the parent diamagnetic molecule.

Calculations were also performed on the dialdehyde (Ic) to test the effect of substituents on the height of the barrier. The computed value of 28.1 kcal mol^{-1} indicates that disubstitution of the 5- and 5'-positions with formyl and presumably also with other electron-withdrawing groups produces only a slight change of the rotational barrier.

TABLE 2

Hyperfine splitting constants in the radical anions of the di- and tri-aryl derivatives (III)—(VIII)

		Aromatic nucleus									
		2-Thienyl			Phenyl			Other			
Compound	Solvent	a_3/G	a_4/G	a_5/G	a_0/G	a_m/G	a_p/G	a_2/G	a_3/G	a_4/G	a_5/G
(III)	DME	5.28	0.57	5.62				3.46		<0.10	0.32
(IV)	DME	4.21	0.77	4.88	2.41	0.31	5.21				
					2.64	0.46					
(V)	HMPA	4.11	1.06	5.60				1.80(2 H)	0.73(2 H)	3.42(N)	
(VI)	HMPA				3.00	0.72 *	5.08	1.93(2 H)	0.86 *(2 H)	3.84(N)	
(VII)	DME	1.20	1.20		1.85	0.42	3.13				
					2.26	0.62					
(VIIIa)	DME	3.16	0.76	3.25	0.88	0.88					
(VIIIb)	DME	3.22	0.71	3.22	1.42(H)	0.71(Me)					

* These splittings may be interchanged

Other Biaryl Derivatives.—The fact that the radical anions of 2,2'-bithienyl as well as of biphenyl[2] are characterized by very large activation energies for intramolecular rotation suggests that in other biaryl derivatives such as (II)—(VI) we should expect the same behaviour.

Attempts to record the spectrum of the radical anion from 3,3'-bithienyl (II) were unsuccessful under all conditions since its reduction with alkali metals gives an e.s.r. spectrum consisting of a single broad line which in a few minutes evolves to the spectrum of 2,2'-bithienyl. This is due to the rearrangement of (II) to the more stable radical anion from (Ia). Whether this rearrangement is inter- or intra-molecular is at present a matter for investigation and e.s.r. spectroscopy, together with a careful investigation of the reaction products, can give useful results allowing a mechanism to be formulated. Similar photochemical interconversions of bithienyls have been thoroughly examined for diamagnetic compounds[28] and the results obtained for the negatively charged radicals should provide useful information for an interesting comparison to be made.

The same rearrangement occurs with 2,3'-bithienyl (III) if working with concentrated samples or keeping the solution in contact with the alkali metal for a long time. However dilute samples of (III) give the corresponding radical anion at −90 °C. The e.s.r. spectrum can be interpreted in terms of the hyperfine splitting constants reported in Table 2; unfortunately the lines are too broad to allow resolutions of the signals from the two possible conformers of (III).

A well resolved spectrum can be obtained from the radical anion of 2-phenylthiophen (IV) which is reasonably stable even at room temperature. The non-equivalence of the *ortho-* and *meta*-protons indicates that the phenyl ring is locked in the e.s.r. time scale, as expected.

The reduction of 4-(2-thienyl)pyridine (V) with alkali metals in DME or THF gives rise to a fairly complicated spectrum because of additional splitting due to the alkali counterion. To avoid the formation of contact ion pairs, the radical was produced in the more polar solvent HMPA, thus leading to considerable simplification of the e.s.r. spectrum. This results from coupling of the unpaired electron with three non-equivalent protons, with two pairs of equivalent protons, and with the pyridine nitrogen (Table 2). Although these constants may lead one to think that the two rings are in rapid rotation, a closer look at the spectrum shows that the lines corresponding to $m_{\alpha,\beta}$ 0 are broader and lower than predicted from the binomial distribution. This suggests that the α- and β-splittings of the pyridyl ring are non-equivalent, even if their difference is not large enough to allow separate signals to be observed.

Table 2 also gives the splitting constants of the radical anion of 4-phenylpyridine (VI), measured in HMPA, which have not previously been reported to the best of our knowledge. In the particular case of (VI), because of the symmetry it is not possible to establish from the e.s.r. spectrum whether the internal rotation is rapid or slow.

For all the derivatives with two different rings, the assignment of the splitting constants has been made by comparison with the parent symmetric diaryls.

---

[28] R. M. Kellog, J. K. Dik, H. van Dziel, and H. Wynberg, *J. Org. Chem.*, 1970, **35**, 2737.

From these results it seems safe to conclude that, generally, biaryls acquire much greater conformational rigidity when they are reduced to the corresponding anion radicals. This behaviour is predicted by theoretical INDO calculations, and is due to the occupation by the unpaired electron of the LUMO of neutral biaryls, which is strongly bonding in the interannular region. The free energies of activation for internal rotation of the aromatic rings, cannot be measured since they are out of the range accessible to e.s.r. spectroscopy.

Triaryls.—Quite a different situation arises in the negative radicals of the triaryls (VII) or (VIII). In these derivatives isomerization may in principle occur *via* simultaneous rotation of both terminal rings (two-ring flip) or the rotation of only one (one-ring flip). The former process may be safely discounted since it is energetically disfavoured. Thus, isomer interconversion will take place by the rotation of one ring only. Since in the transition state conjugation of this ring with the other two is prevented for geometrical reasons, the barrier to rotation will be approximately represented by the difference between the energy of the negatively charged triaryl and the sum of the energy of the appropriate diaryl anion radical, and that of the remaining monoaryl, which is expected to be much smaller than for internal rotation of a diaryl radical. INDO calculations performed on the planar and perpendicular forms of (VII) and (VIIIa), give energy barriers of only 10.04 and 7.49 kcal mol^{-1}, respectively.

A check on the reliability of these results comes from the e.s.r. spectrum of the anion radical from 2,5-diphenylthiophen (VII) which shows restricted rotation of the phenyl rings up to 60 °C, as indicated by the non-equivalence of the *ortho*- and *meta*-protons (see Table 2). Above this temperature selective line broadening is observed. The interconversion process could not be followed to much higher temperatures because the radical decays; however a rough estimate of the free energy of activation $\Delta G^{\ddagger}$ gives 11 ± 1 kcal mol^{-1}.

Since INDO calculations predict reasonably well the experimental barrier to rotation of (VII), we might expect similar agreement in the case of *p*-di-(2-thienyl)-benzene (VIIIa). The room temperature e.s.r. spectrum of this radical can be interpreted in terms of four sets of hyperfine splitting constants, three of which come from pairs of equivalent protons and the other from four equivalent protons. The last set has been assigned to the phenyl hydrogens which could be equivalent as a result of rapid rotational averaging. Surprisingly they remain equivalent at temperatures as low as −100 °C. This can be explained by admitting either that the barrier to rotation is lower than *ca.* 5 kcal mol^{-1}, or that the difference in the hyperfine splittings between the two sets of phenyl protons is smaller than the linewidth. Since there seems to be no reasonable justification for such a small value of $\Delta G^{\ddagger}$, we favour the second hypothesis.

Attempts to answer this question with the aid of the dimethyl-substituted derivative (VIIIb) were unsuccessful. In this case an e.s.r. spectrum consisting of the superposition of two different isomeric species should be observed. In practice only one isomer was detected, probably that with the methyl groups *cis* to the sulphur atom of the thiophen rings.[5]

Financial support from C.N.R., Rome, is gratefully acknowledged (G. F. P. and M. T.).

[7/880 *Received, 20th May,* 1977]