# Radical Anions of Substituted Thienothiophens

By **Gian Franco Pedulli,*** Istituto di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna, Italy
Marcello Tiecco,* Istituto di Chimica Organica dell'Università, Via Amendola 173, 70126 Bari, Italy
Angelo Alberti and **Giorgio Martelli,** Laboratorio del C.N.R. per lo Studio dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, Ozzano Emilia, Italy

The e.s.r. spectra of the radical anions of carbonyl-, nitro-, and cyano-derivatives of thieno[3,2-*b*]thiophen and thieno[2,3-*b*]thiophen have been investigated in order to compare their properties with those of the corresponding substituted thiophens. From an examination of the hyperfine splitting constants it is concluded that in the case of thieno[3,2-*b*]thiophen the unpaired electron is delocalized over the whole molecule, while in thieno[2,3-*b*]thiophen the condensed thieno-group is scarcely involved. Nitrogen coupling constants for (II) and (III), as well as the proton splittings in the mixed terms of ketones (I) indicate that thieno[3,2-*b*]thiophen has a delocalization power greater than the thieno[2,3-*b*]thiophen which in its turn is slightly more efficient than thiophen.

THE study by e.s.r. spectroscopy of radicals containing the thiophen ring with regard to their stability, electronic distribution,[1] and conformational properties [2-4] has been the subject of many recent papers. In contrast, little attention has been devoted to the investigation of the properties and reactivity of radicals of condensed thiophens. E.s.r. studies have been recently carried

	Ketones (I)	Nitro-compounds (II)	Nitriles (III)
a;	R^1COR^1	a; R^1NO_2	a; R^1CN
b;	R^1COR^2	b; R^3NO_2	b; R^3CN
c;	R^2COR^2	c; R^4NO_2	c; R^4CN
d;	R^3COR^3		
e;	R^4COR^4		
f;	R^1COR^3		
g;	R^1COR^4		
h;	R^3COR^4		
i;	R^3COR^5		
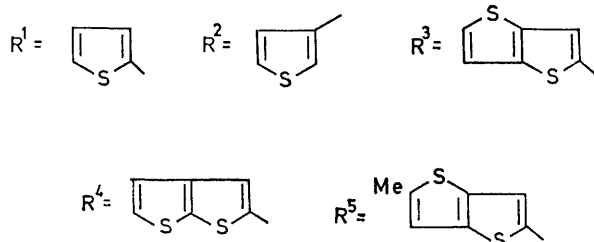
out on the anions of thieno[3,2-*b*]thiophen-2,5-dicarbaldehyde [4] and of some benzodithiophens,[5] the anion and cation of thieno[3,2-*b*]thiophen,[5,6] and the cation of a dithienothiophen.[6] The reactivity of the thieno[3,2-*b*]- and thieno[2,3-*b*]-thiophen towards substitution by free radicals has also been studied.[7]

We report here the results of an e.s.r. investigation on some carbonyl-, nitro-, and cyano-derivatives of the two isomeric thienothiophens carried out in order to compare their properties with those of the corresponding substituted thiophens.

EXPERIMENTAL

The ketones of the two thienothiophens were obtained by reaction of the appropriate aromatic substrate with a carboxylic acid in the presence of P_2O_5 following the general procedure reported for compound (Id). The yields were in every case of the order of 50—60%, depending on the acid employed.

Bis-2-thieno[3,2-b]*thienyl Ketone* (Id).—A mixture of thieno[3,2-*b*]thiophen [8] (0·5 g), thieno[3,2-*b*]thiophen-2-carboxylic acid [8] (0·5 g), and P_2O_5 (0·32 g) were refluxed in benzene (20 ml) for 5 h. The mixture was poured onto water and the two layers separated. The organic solution was washed with a dilute solution of sodium hydroxide and with water. After drying (Na_2SO_4), the solvent was evaporated and the residue was chromatographed over silica gel using light petroleum (b.p. 40—70 °C)–acetone (4 : 1) as eluant. The *ketone* was eluted after the unchanged thienothiophen and was further purified by crystallization from benzene, m.p. 190—191 °C (Found: C, 51·6; H, 1·95; S, 42·05. $C_{13}H_6OS_4$ requires C, 50·95; H, 1·95; S, 42·1%).

2-(5-Methyl)thieno[3,2-b]*thienyl 2-Thieno*[3,2-b]*thienyl Ketone* (Ii).—This *compound* was obtained from thieno-[3,2-*b*]thiophen-2-carboxylic acid [8] and 2-methylthieno-[3,2-*b*]thiophen,[9] m.p. 161—162 °C (from benzene–light petroleum) (Found: C, 53·0; H, 2·45; S, 40·3. $C_{14}H_8OS_4$ requires C, 53·2; H, 2·5; S, 40·0%).

Bis-2-thieno[2,3-b]*thienyl Ketone* (Ie).—This *compound* was prepared from thieno[2,3-*b*]thiophen [10] and thieno-[2,3-*b*]thiophen-2-carboxylic acid,[10] m.p. 186—187 °C (from benzene–light petroleum) (Found: C, 50·9; H, 1·9; S, 42·1%).

2-Thieno[3,2-b]*thienyl 2-Thieno*[2,3-b]*thienyl Ketone* (Ih). —The starting products for the synthesis of this *compound* were thieno[2,3-*b*]thiophen and thieno[3,2-*b*]thiophen-2-carboxylic acid, m.p. 169—170 °C (from acetone) (Found: C, 50·9; H, 1·95; S, 41·95%).

2-Thieno[3,2-b]*thienyl 2-Thienyl Ketone* (If).—The reaction was carried out using thieno[3,2-*b*]thiophen-2-carboxylic acid (2 g), thiophen (5 ml), P_2O_5 (1·3 g), and benzene (20 ml). The *product* (2·1 g) was crystallized from

[1] L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, **101**, 10.
[2] P. Cavalieri d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Letters*, 1969, 4179.
[3] A. Hudson and J. W. E. Lewis, *Tetrahedron*, 1970, 4413.
[4] L. Lunazzi, G. F. Pedulli, M. Tiecco, C. A. Veracini, and C. Vincenzi, *J.C.S. Perkin II*, 1972, 751.
[5] L. Lunazzi, G. Martelli, G. Placucci, and M. Tiecco, *J. Chem. Soc. (B)*, 1971, 1820.
[6] L. Lunazzi, G. Placucci, and M. Tiecco, *Tetrahedron Letters*, 1972, 3847.

[7] P. Spagnolo, L. Testaferri, M. Tiecco, and G. Martelli, *J.C.S. Perkin I*, 1972, 93.
[8] Ya. L. Goldfarb, V. P. Litvinov, and S. A. Ozolin, *Isvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1965, 510 (*Chem. Abs.*, 1965, **63**, 595f).
[9] L. Brandsma and D. Schuijl-Laros, *Rec. Trav. chim.*, 1970, **89**, 110.
[10] S. Gronowitz and B. Persson, *Acta Chem. Scand.*, 1967, **21**, 812.

methanol, m.p. 113—114 °C (Found: C, 52·7; H, 2·45; S, 38·1. $C_{11}H_6OS_3$ requires 52·8; H, 2·4; S, 38·4%).

2-*Thieno*[2,3-b]*thienyl* 2-*Thienyl* *Ketone* (Ig).—The *product* was obtained from thiophen and thieno[2,3-b]thiophen-2-carboxylic acid in the ratio reported above, m.p. 101—102 °C (from methanol) (Found: C, 52·9; H, 2·5; S, 38·3%).

2-*Cyanothieno*[3,2-b]*thiophen* (IIIb).—A mixture of 2-bromothieno[3,2-b]thiophen [11] (2·3 g), cuprous cyanide (1·2 g), and dimethylformamide (7 ml) was stirred and refluxed for 12 h. The resulting mixture was poured into a solution of hydrated ferric chloride (40 g), concentrated hydrochloric acid (10 ml), and water (60 ml) and warmed at 60—70 °C for 20 min. After cooling, benzene was added and the two layers were separated. The *residue* (1·9 g) was crystallized from ethanol, m.p. 113—114 °C (Found: C, 50·9; H, 1·85; N, 8·45; S, 38·65. C_7H_3NS requires C, 50·9; H, 1·85; N, 8·45; S, 38·8%).

2-*Cyanothieno*[2,3-b]*thiophen* (IIIc).—This *compound* was prepared from 2-bromothieno[2,3-b]thiophen [11] following the procedure described above, m.p. 64—65 °C (from ethanol) (Found: C, 50·85; H, 1·95; N, 8·35; S, 39·0%).

The dithienyl ketones (Ia),[12] (Ib),[13] and (Ic),[14] 2-cyanothiophen (IIIa),[15] 2-nitrothiophen (IIa),[16] 2-nitrothieno-[3,2-b]thiophen (IIb),[17] and 2-nitrothieno[2,3-b]thiophen (IIc) [17] were prepared as described in the literature.

Radicals.—Ketyl radicals were prepared from the corresponding ketones by conventional reduction in dimethoxyethane (DME) with potassium and by photolysis in deoxygenated solution of a mixture of sodium methoxide, methanol, and DME in the ratio 1 : 3 : 4. The latter method allows well resolved spectra to be obtained for a reasonably large range of temperatures without the further complication due to the presence of additional hyperfine structure from the alkali metal. The radicals appear from a few seconds to several minutes after starting to irradiate depending on the ketone. The addition of DME is necessary since some of the ketones are almost completely insoluble in alcohol; furthermore, the presence of DME is useful even when the ketones are soluble, since it has been found to increase the stability of the radicals.

The nitro-anion radicals were produced by treating the corresponding nitro-derivatives with potassium t-butoxide in dimethyl sulphoxide (DMSO) and by the photolytic method described above.

The radical anions of the cyano-derivatives had to be generated, because of their very low stability, directly in the e.s.r. sample tube on the surface of a sodium–potassium alloy at ca. −100 °C using a 1 : 2 mixture of DME and tetrahydrofuran as solvent.

Spin Density Calculations.—MO Spin density calculations were carried out on the radicals (I)—(III) using the McLachlan method.[18] The necessary parameters for the carbonyl ($h_O = 1·5$, $K_{CO} = 1·6$, $K_{CC'} = 0·9$), nitro ($h_N = 2·2$, $h_O = 1·4$, $K_{NO} = 1·67$, $K_{CN} = 1·2$), and cyano ($h_N = 1·0$, $K_{CN} = 2·0$, $K_{CC'} = 0·9$) substituents were taken from the work by Rieger and Fraenkel,[19] while those for the sulphur atom are those we used for a number of thiophen deriva-

tives [1] ($h_S = 1·0$, $K_{CS} = 0·86$). No attempt to deal with the d model for the sulphur atom has been made.

RESULTS

An investigation of the radical anions of the three dithienyl ketones (Ia—c), produced by electrolytic reduction, was reported previously [20] and we give here only the hyperfine splitting constants obtained in MeOH–DME since they are strongly solvent dependent.

The room temperature e.s.r. spectra of the symmetric ketyls of the two thienothiophens (Id and e) are shown in Figure 1. They can be straightforwardly interpreted in terms of the three hyperfine splitting constants reported in the Table, arising from the coupling of the unpaired electron with three pairs of equivalent protons. The smallest splitting in the radical anion of (Ie) can be resolved only by using a low modulation amplitude and scanning the spectrum slowly. Both spectra look asymmetric as the high
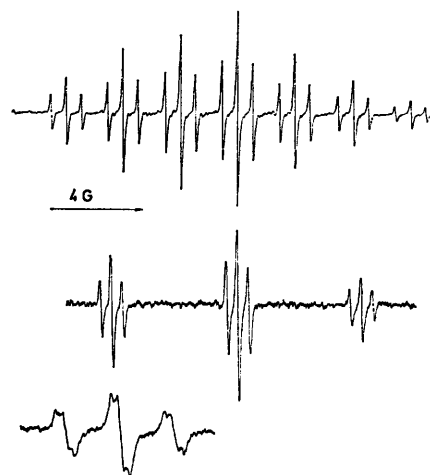

FIGURE 1 Room temperature e.s.r. spectra of the ketyls from bis-2-thieno[3,2-b]thienyl ketone (Id) (upper) and bis-2-thieno-[2,3-b]thienyl ketone (Ie) produced photolytically in MeOH–DME

field lines are broader than the low field ones. This effect is not due to a linewidth dependence on the nuclear quantum number as may appear by simple spectral inspection. Actually, upon decreasing the temperature, the asymmetry becomes more evident and at ca. −10 °C the high field part of the spectra splits into new lines indicating the presence of two species having similar hyperfine splittings and slightly different g factors, which have been identified as two of the rotational isomers of these radicals. The assignment of the structures to these conformers and the determination of the rotational barriers around the aryl–carbonyl bond will be reported in a future paper.[21]

The spectra of the symmetric ketyl radicals from compounds (If—h) are more complex because of the presence of

[11] A. Bugge, *Acta Chem. Scand.*, 1969, **23**, 2704.
[12] H. D. Hartough and A. I. Korak, *J. Amer. Chem. Soc.*, 1947, **69**, 3098.
[13] S. Gronowitz, *Arkiv Kemi*, 1958, **12**, 533.
[14] S. Gronowitz and B. Eriksson, *Arkiv Kemi*, 1963, **21**, 335.
[15] R. J. Meltzer, A. D. Lewis, and J. A. King, *J. Amer. Chem. Soc.*, 1955, **77**, 4062.
[16] B. Östman, *Acta Chem. Scand.*, 1968, **22**, 1687.

[17] F. Challanger and R. Emmott, *J. Inst. Petroleum*, 1948, **34**, 922.
[18] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[19] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609.
[20] P. Cavalieri d'Oro, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Boll. sci. Fac. Chim. ind. Bologna*, 1969, **27**, 133.
[21] M. Guerra, G. Martelli, G. F. Pedulli, and M. Tiecco, to be published.

six nonequivalent protons; however they could be interpreted and the relative hyperfine splitting constants measured in MeOH–DME are reported in the Table. In every case the low temperature spectra showed evidence of the presence of conformational isomers.

The ketones have also been reduced with potassium in DME; under these conditions they are known to give rise to contact ion pairs formed by the ketyl anion and the alkali

measured coupling constants are collected in the Table together with those of the thiophen derivatives. The anion radical of 2-nitrothiophen produced electrolytically has been described by Lucken,[23] while the 2-cyanothiophen radical anion has not been studied previously. The two methods we used to form radicals from the nitro-compounds give spectra which are much better resolved than those obtained by reduction by alkali metals or by electrolysis. All

Hyperfine splitting constants (10^{-4}T) of the radical anions from (I)—(III)

Aromatic nucleus

Compound	Solvent	2-Thieno[3,2-b]-thienyl			2-Thieno[2,3-b]-thienyl			2-Thienyl			3-Thienyl			a_N
		a_3	a_5	a_6	a_3	a_4	a_5	a_3	a_4	a_5	a_2	a_4	a_5	
(Ia)	MeOH–DME							4·85	1·06	4·11				
	DME							4·32	0·89	3·82				
(Ib)	MeOH–DME							5·49	1·26	4·85	4·18	0·90	0·54	
(Ic)	MeOH–DME										5·43	1·03	0·65	
(Id)	MeOH–DME	4·90	2·43	0·65										
	DME	4·46	2·33	0·60										
(Ie)	MeOH–DME				5·46	0·068	0·49							
	DME				5·02	0·11	0·46							
(If)	MeOH–DME	5·30	2·70	0·72				4·19	0·92	3·49				
	DME	5·10	2·72	0·68				3·90	0·84	3·36				
(Ig)	MeOH–DME				5·52	0·064	0·50	4·65	1·04	3·96				
	DME				5·20	0·11	0·46	4·23	0·94	3·73				
(Ih)	MeOH–DME	5·17	2·59	0·69	4·88	<0·08	0·44							
	DME	4·94	2·63	0·67	4·62	0·094	0·43							
(Ii)	MeOH–DME	4·88	2·48	0·64										
		4·99	(4H)	(2H)										
(IIa)	MeOH–DME							5·72	1·21	4·74				12·04
	DMSO							5·72	1·24	4·73				9·74
(IIb)	MeOH–DME	6·48	2·96	0·78										11·15
	DMSO	6·10	2·85	0·80										8·45
(IIc)	MeOH–DME				6·71	<0·1	0·56							11·91
	DMSO				6·65	<0·1	0·55							9·60
(IIIa)	DME–THF							5·69	0·88	7·56				1·87
(IIIb)	DME–THF	5·30	5·30	1·00										1·79
(IIIc)	DME–THF				4·77	0·43	0·43							1·85

metal positive ion, as revealed by the presence of electron spin density on the alkali ion. In the present cases the potassium hyperfine splitting ranges from 0.21×10^{-4} to 0.26×10^{-4}T at room temperature, being largest for ketone (Ia), and shows a positive temperature dependence. The proton splittings (Table) are considerably smaller than the corresponding values for MeOH–DME mixtures. This behaviour is expected since, in protic solvents such as alcohols, the formation of a hydrogen bond between the carbonyl group and the solvent tends to make the proton splittings larger by stabilizing resonance structures in which the negative charge is localized on the ketyl oxygen atom.[22]
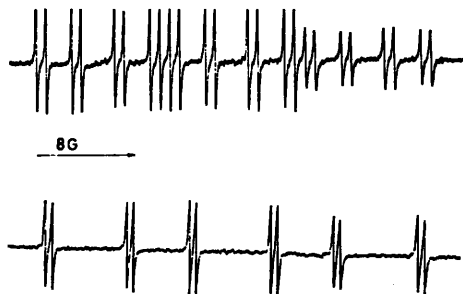

8G

FIGURE 2   Room temperature e.s.r. spectra of the radical anions of 2-nitrothieno[3,2-b]thiopen (IIb) (upper) and 2-nitrothieno-[2,3-b]thiophen (IIc) produced photolytically in MeOH–DME

The spectra of the radical anions of the nitro- and cyano-thienothiophens are shown in Figures 2 and 3 and the

have the familiar linewidth dependence on the nitrogen nuclear quantum number even at room temperature because of the large anisotropy of the nitrogen hyperfine
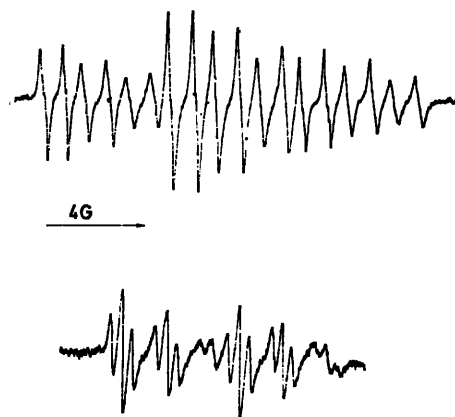

4G

FIGURE 3   E.s.r spectra of the radical anions of 2-cyano-thieno[3,2-b]thiophen (IIIb) (upper) and 2-cyanothieno-[2,3-b]thiophen (IIIc) recorded at −80 °C in DME–THF

tensor. This anisotropy is not so large in the radical anions of the cyano-derivatives; however their spectra are still highly asymmetric because of the high viscosity of the

[22] K. Nakamura and N. Hirota, Chem. Phys. Letters, 1969, 3, 137.

[23] E. A. Lucken, J. Chem. Soc. (A), 1966, 991.

solvent at the temperature at which they have been recorded. It is also evident from the barely resolved hyperfine structure due to the alkali metal that the cyano-radicals are present as ion pairs.

DISCUSSION

The assignment of the hyperfine splitting constants of the ketyls of the dithienones (Ia—c) has been discussed previously.[20]

For the radical anion from the ketone (Id), spin density calculations or simple considerations based on the more important resonance structures show that the two larger coupling constants should be due to 3- and 5-H. To distinguish between these two positions we prepared ketone (Ii) which has a 5-Me group. The methyl splitting of 2.48×10^{-4} T indicates that the larger coupling is attributable to 3-H.

In the ketyl from compound (Ie) the larger splitting constant can similarly be assigned to 3-H. As the remaining splittings are both very small, we did not try to assign them experimentally; however, since MO calculations give the smaller spin density on C-4, the 0.068×10^{-4} T splitting was attributed to this position.

In the asymmetric ketyls from compounds (If—h) the assignment was made by analogy with the symmetric derivatives, because the hyperfine splitting constants of a given aromatic ring do not experience large variations when going to the mixed ketyls. Further, each constant changes in proportion to the other of the same ring, so that their identification becomes straightforward.

The assignment of the hyperfine splittings for 2-nitrothiophen (IIa) was made by Lucken[23] by studying various methylated derivatives and in the two nitrothienothiophens (IIb and c) by analogy with the ketyls. Spin density calculations confirm this assignment.

In the cyano-derivatives (III) a problem arises in assigning the thiophen splitting as the two larger constants of (IIIb) and the two smaller of (IIIc), whose attribution could lead to some ambiguity, are equal. In the 2-cyanothiophen radical anion, MO calculations give the greater spin density on C-5, at variance with the ketyls and nitro-derivatives where the unpaired electron is more localized on C-3. This behaviour however is not completely unexpected, since it has been found already in the 2,2'-dithienyl anion radical where the theoretical assignment was experimentally verified by deuterio-substitution.[1] In general it seems that in thiophens monosubstituted at C-2 by a nitro,[23] carbonyl,[20] or nitroxide function[24] or by a diarylmethyl group,[1] which can greatly delocalize the unpaired electron, the spin density tends to be larger on C-3 than on C-5; the reverse occurs with other substituents. A considerable redistribution of spin density is also evident in the cyano-thienothiophens with respect to the corresponding nitro and ketyl radicals.

The values of the hyperfine splitting constants in the derivatives (I)—(III) clearly indicates different behaviour of the two isomeric thienothiophens. In the radical anions of the 2-substituted thieno[3,2-b]thiophen, both the condensed thiophen rings contribute to the delocalization of the unpaired electron as predicted on the basis of the limiting structures a—d; structure c, where the odd electron is located on C-6a, probably does not contribute appreciably to the resonance system because the loss of aromaticity of both rings is not counterbalanced
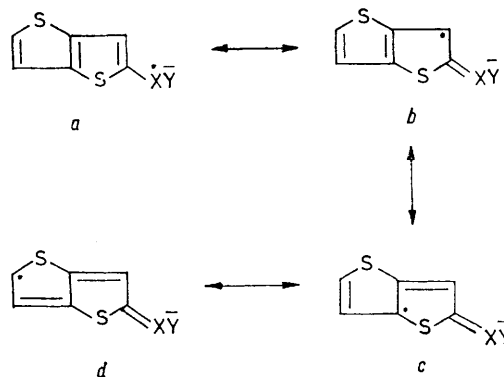
by extended conjugation as in d. This is supported by the small spin density on C-6a predicted by MO calculations when compared with the values for the corresponding position in the thiophen derivatives [for instance 0.0603 and 0.1286 in the ketyls from (Id) and (Ia)].

In the derivatives of thieno[2,3-b]thiophen the small coupling constants of 4- and 5-H indicate that the condensed thieno-group is hardly involved in the delocalization of the unpaired electron. Of the possible limiting structures e—g, f gives rise to the large value of a_3^H, while the importance of structure g is expected to be
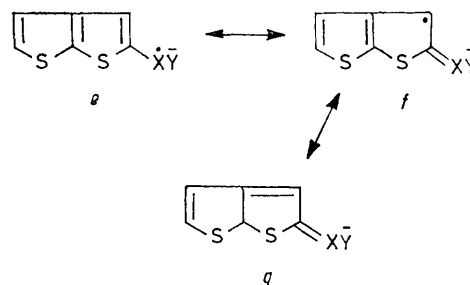
very limited for the same reasons discussed previously for structure c. MO Calculations predict very small spin density (0.0533) on the carbon adjacent to the sulphur atoms in the ketyl from (Ie).

This different behaviour is also reflected in the chemical reactivity of the two thienothiophen rings towards free radicals. The isomer distribution data for the phenylation of the two heterocycles have been explained by utilizing considerations similar to those

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reported above,[7] on the assumption that the intermediate σ complexes represent reasonable transition states for homolytic substitution.

The hyperfine splitting constants also give useful information on the relative electron-withdrawing ability of the thiophen and thienothiophen rings. An increase of the proton splitting of a given aromatic nucleus when going from a symmetric to an asymmetric ketyl means more pronounced ability to delocalize the unpaired electron with respect to the other ring. When dealing with the nitro- and cyano-derivatives similar information may be obtained from the nitrogen splittings which may be assumed to be roughly proportional to the spin density on the nitro- or cyano-groups

In every case the electron-withdrawing power is greater for the 2-thieno[3,2-b]thienyl than for the 2-thieno[2,3-b]thienyl group, which in its turn can delocalize the odd electron slightly better than 2-thienyl and much better than 3-thienyl. This trend is not surprising since in thieno[3,2-b]thienyl both rings contribute to the delocalization of the unpaired electron, while the limited participation of the second ring to the π resonance system explains the similarity of behaviour of the thieno[2,3-b]thienyl with the 2-thienyl group.

Of course, the greater the electron-withdrawing ability of these aromatic nuclei the greater should be the double-bond character of the link with the substituent; consequently the energy barrier to rotation around this bond should increase with the delocalization power of the heterocyclic ring. This obviously cannot be tested experimentally for the cyano- and nitro-radical anions but it is possible for ketyls where rotation gives rise to distinct conformational isomers. This kind of investigation is being carried out by analysing the line shape variations with temperature of the e.s.r. spectra of the ketyls; [21] the experimental barriers thus determined change with the nature of the aromatic rings and have been found to be proportional to their delocalization power.