An Electron Spin Resonance Study of Ring Inversion in the Radical Anions of *peri*-Bridged Naphthalenes and Singly Bridged Biphenyls

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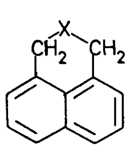
The radical anions of 2,3-dihydrophenalene, 1*H*,3*H*-naphtho[1,8-*cd*]pyran and 6,7-dihydro-5*H*-dibenzo[*a,c*]-cycloheptene were generated by alkali metal reduction and their e.s.r. spectra recorded at several temperatures. Symmetric line width broadening due to the modulation of the β-axial and equatorial proton splittings were observed. By analysing the line shape variations with temperature, the activation parameters for the inversion of the aliphatic ring could be determined. A comparison of the experimental activation energies for the radical anions with those estimated by force field calculations on the parent compounds shows that the addition of an unpaired electron to the π-system gives rise to a large change in the inversion barrier in the bridged biphenyl, while no variation seems to occur in the bridged naphthalene. This behaviour is rationalized in terms of the π-resonance energies of the open and closed shell systems.

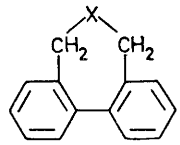
WE have been recently concerned with dynamic e.s.r. studies of flexible aromatic radical anions in order to examine how the presence of the additional electron modifies the energy barriers to rotation compared with the analogous process in the corresponding neutral molecules. In mono- and di-arylketyls[1] and in the radical anions of biaryls[2] these barriers were found to be much greater than in the diamagnetic precursors. A simple explanation of this effect was given in terms of the occupation, by the extra electron, of the lowest unoccupied π-molecular orbital (LUMO) which has, in both classes of radical, strong bonding character around the link about which rotation occurs. When the LUMO is filled by the unpaired electron, the increased conjugation between the two groups rotating about each other, induces a flattening of nonplanar molecules in their ground state and more generally a sharp increase in the energy barriers to rotation.

In this paper we deal with the dynamics of ring inversion in the radical anions of some substituted naphthalenes and biphenyls in order to study whether and to what extent conformational processes of this kind are influenced by the addition of the unpaired electron to the π-system.

Attempts to examine the radicals from the six derivatives (I)—(VI) were made; however only three of them, (I), (II), and (IV), gave the corresponding anion radicals without decomposition.

N.m.r. techniques have been applied unsuccesfully to study the dynamics of ring inversion in six-membered ring *peri*-substituted naphthalenes.[3] Even in the selenium analogue of (I)—(III), in spite of the large size of the selenium atom, the methylene protons gave still a singlet at temperature as low as −100°. E.s.r. spectroscopy on the other hand proved to be more convenient for studying conformational processes of this kind because of the intrinsically shorter time scale involved. The dynamics of the radical anion of 1,2,3,6,7,8-hexahydropyrene has been extensively investigated by different workers, though with contradictory results. de Boer *et al.*[4] report an activation energy of 10.0 kcal mol^{-1} while Claridge *et al.*[5] give a much smaller value, 6.4 kcal mol^{-1}. The latter group also recorded some e.s.r. spectra of the radical anion of 2,3-dihydrophenalene (I); however no accurate lineshape analysis was performed in this case and only an approximate estimate (7.5 ± 1.5 kcal mol^{-1}) of the activation energy of ring inversion was reported.


(I) X = CH$_2$
(II) X = O
(III) X = S


(IV) X = CH$_2$
(V) X = O
(VI) X = S

More attention has been paid to bridged biphenyls since the relatively large energy barriers to inversion allowed these compounds to be conveniently studied by dynamic n.m.r. spectroscopy.[6-8] Experimental activation energies were determined for both the oxepin (V) and the thiepin (VI). Kurland *et al.*[7] found E_a 9.2 ± 1 and 16.1 ± 0.3 kcal mol^{-1} respectively for (V) and (VI), and Sutherland and Ramsay[8] report $\Delta G^{\ddagger}$ 16.0 kcal mol^{-1} for the thiepin (VI) in CDCl$_3$. These results agree well with the calculated potential energy barriers of 9 and 17 kcal mol^{-1} reported by Mislow *et al.*[9] The latter authors give also an estimate of the barrier for the dibenzocycloheptene (IV) as 13 kcal mol^{-1}. Although this compound

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[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] P. Cavalieri d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Letters*, 1969, 4179; M. Guerra, G. F. Pedulli, and M. Tiecco, to be published.

[3] A. Biezais-Zirnis and A. Fredga, *Acta Chem. Scand.*, 1971, **25**, 1171.

[4] F. W. Pijpers, M. R. Arick, M. P. Hendriks, and E. de Boer, *Mol. Phys.*, 1971, **22**, 781.

[5] R. F. C. Claridge, B. M. Peake, and R. M. Golding, *J. Magnetic Resonance*, 1972, **6**, 29.

[6] M. Oki, H. Iwamura, and N. Hagakawa, *Bull. Chem. Soc. Japan*, 1963, **36**, 1542; 1964, **37**, 1865.

[7] R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426.

[8] I. O. Sutherland and M. V. J. Ramsay, *Tetrahedron*, 1965, **21**, 3401.

[9] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

has not yet been studied by dynamic n.m.r. because of the complexity of its spectrum, it is gratifying that in the 6-$(CO_2Et)_2$ derivative of (IV) E_a was found to be 13.7 kcal mol^{-1} in good agreement with the calculated potential energy of activation.[8]

Dynamic e.s.r. studies have been reported only for a six-membered ring bridged biphenyl by Adam[10] who found an activation energy of 4.6 kcal mol^{-1} in the radical anion of 9,10-dihydrophenanthrene.

EXPERIMENTAL

2,3-Dihydrophenalene (I) was a commercial product purified by crystallization from ethanol. 1*H*,3*H*-naphtho-[1,8-*cd*]pyran (II),[11] the thiopyran (III),[3] 6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene (IV),[12] 5,7-dihydrodibenzo[*c,e*]-oxepin (V),[11] and the corresponding sulphur analogue (VI)[13] were prepared according to established methods and have physical properties in agreement with those in the literature.

The radical anions of the naphthalene derivatives were generated by reduction with sodium–potassium alloy in deoxygenated solutions of a 1 : 2 mixture of dimethoxyethane (DME) and tetrahydrofuran (THF). The substituted biphenyls were reduced with Na or K in pure THF or in pure DME.

The temperature of the sample was controlled using standard variable temperature accessories and measured before and after each scan by means of a chromel–alumel thermocouple placed in the e.s.r. cavity.

RESULTS

Bridged Naphthalenes.—The room temperature e.s.r. spectrum of the radical anion of (I) may be interpreted on the basis of the coupling of the unpaired electron with five different groups of protons, *i.e.* three sets of two aromatic protons, two γ-protons, and four β-protons. The last give a triplet with an intensity ratio 1 : 4 : 1 split by 10.90 G. The two lines corresponding to $M_\beta \pm 1$ are completely washed out by modulation of the β-methylene proton splittings due to rapid interconversion between the axial and equatorial positions. The apparent splitting is therefore the sum of $a_{\beta,ax}$ and $a_{\beta,eq}$. The measured hyperfine coupling constants shown in Table 1 are in agreement with those in the literature.[5] The aromatic proton splittings were assigned to the ring positions by analogy with the attribution for the radical anion of 1,8-dimethylnaphthalene.[14]

As the temperature is lowered the rate of ring inversion is further reduced so that the four β-methylene protons are resolved to a triplet of triplets. At $-70°$ the two γ-protons give distinct axial and equatorial splittings, and the whole spectrum can be interpreted in terms of seven hyperfine coupling constants. The splittings from the aromatic hydrogens are slightly temperature dependent as shown in Table 1.

The radical anion from the pyran (II) was stable only below $-50°$. The corresponding e.s.r. spectrum, shown in Figure 1, is much simpler than in the case of 2,3-dihydrophenalene because of the absence of the γ-methylene protons. It results from the coupling of the unpaired electron with only three sets of equivalent protons, since the 2,7- and 3,6-splittings are accidentally degenerate. Also in this case the four methylene hydrogens give a 1 : 4 : 1 triplet separated by $a_{ax} + a_{eq}$. On lowering the temperature new lines corresponding to $M_{\beta,ax}$ and $M_{\beta,eq} = 0$ appear in the e.s.r. spectrum. The low temperature spectra can be properly simulated only by assuming partial removal of the degeneracy of the smaller splittings due to the aromatic protons. The values used for simulation are reported in Table 1.

TABLE 1

Hyperfine splitting constants (G) of the radical anions from (I), (II), and (IV).

Compound	T (°C)	a_2	a_3	a_4	a_5	$a_{\beta,ax}$	$a_{\beta,eq}$	$a_{\gamma,ax}$	$a_{\gamma,eq}$
(I)	25	1.56	2.00	4.52		5.45		0.44	
	−70	1.56	1.92	4.56		8.72	2.22	0.55	0.37
(II)	−71	1.80	1.80	4.68		5.50			
	−94	1.72	1.84	4.68		8.34	2.66		
(IV)	25	2.82	0.55	5.32	0.42	1.52		0.42	
	−60	2.82	0.55	5.32	0.42	2.04	1.00	0.42	

Attempts to prepare the negative radical from the thiopyran (III) were unsuccesful as, in every case, the e.s.r. spectrum of the radical anion of 1,8-dimethylnaphthalene was obtained. To avoid the rupture of the sulphur bridge the reaction between (III) and the sodium–potassium alloy was carried out at $-100°$; under these conditions an e.s.r. spectrum probably due to the radical anion of (III) was

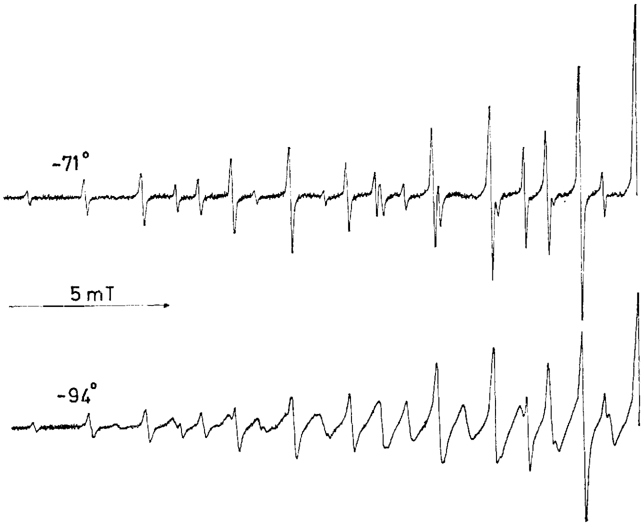

FIGURE 1 E.s.r. spectra of the radical anion from (II) in the intermediate and slow exchange regions

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[10] F. C. Adam, *Canad. J. Chem.*, 1971, **49**, 3524.

[11] A. J. Weinheimer, S. W. Kantor, and C. R. Hauser, *J. Org. Chem.*, 1953, **18**, 801.

[12] A. C. Cope and R. D. Smith, *J. Amer. Chem. Soc.*, 1956, **78**, 1012.

[13] W. E. Truce and D. D. Emrik, *J. Amer. Chem. Soc.*, 1956, **78**, 6130.

[14] R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, 1969, **51**, 1765.

first observed. However it rapidly decayed and after a few minutes the anion of 1,8-dimethylnaphthalene was the only radical present.

Bridged Biphenyls.—The radical anion of 6,7-dihydro-5*H*-dibenzocyclo[*a,c*]heptene prepared by potassium reduction in DME is stable over a wide temperature range. The room temperature e.s.r. spectrum can be easily analysed in terms of the five hyperfine splitting constants reported in Table 1. Symmetrical line width broadening due to the exchange of the β-methylene splittings has been observed between 15 and −60°. Below the latter temperature different axial and equatorial β-couplings can be measured as reported in Table 1. The γ-methylene protons are always equivalent as can be predicted from molecular symmetry. The assignment of the hyperfine splittings has been made by analogy with those for the radical anions of 2,2′-dialkylbiphenyls.[15]

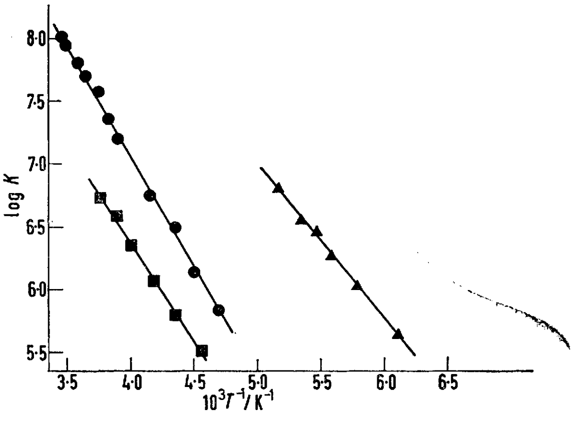


FIGURE 2 Arrhenius diagrams of the rate constants to ring inversion for the radical anions from: ■, (I); ▲, (II); ●, (IV)

The reduction with Na or K of 2,7-dihydrodibenzo[*c,e*]-oxepin (V) gives an e.s.r spectrum showing coupling of the unpaired electron with five pairs of protons. The measured hyperfine splittings at −30° are 0.49, 0.63, 2.96, 3.81, and 4.61 G and are coincident with those of the radical anion of phenanthrene.

The thiepin (VI) derivative, on the other hand, is transformed by metal reduction into the radical anion of 2,2′-dimethylbiphenyl.[15] Decomposition of compounds (V) and (VI) could not be avoided even working at very low temperatures.

Dynamics of Ring Inversion.—Quantitative information on the dynamics of ring inversion in the anion radicals from (I), (II), and (IV) has been obtained by analysing the spectral shape variations with temperature using the density matrix theory.[16] In every case the dynamic process may be described by a simple two-jump model involving two equally populated sites. The determination of the rate constants was made by visually fitting the experimental spectra to those simulated by a computer program already described.[17] The results are graphically summarized in Figure 2, which shows the Arrhenius diagrams for the three radicals examined. Table 2 collects the activation parameters and the thermodynamic constants for the activated complex obtained from the Eyring equation using a unitary transmission coefficient. These quantities, together with their standard deviations, have been calculated using standard least-squares procedures.

TABLE 2

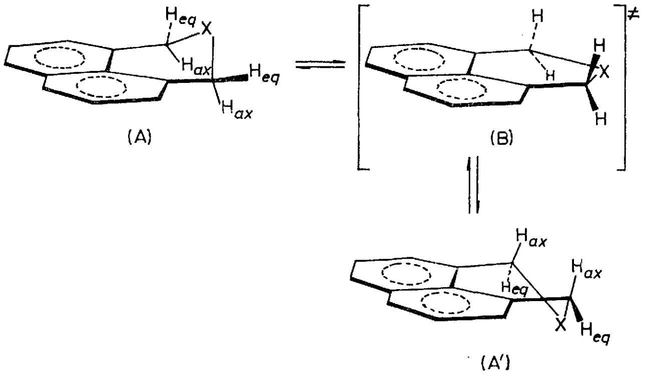
Activation parameters for the ring inversion in the radical anions of (I), (II), and (IV)

Compound	E_a/ kcal mol^{-1}	log A	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}
(I)	7.19 ± 0.16	12.65 ± 0.14	6.72 ± 0.16	−2.17 ± 0.67
(II)	5.47 ± 0.16	12.96 ± 0.60	5.12 ± 0.17	−0.22 ± 0.04
(IV)	8.07 ± 0.13	14.11 ± 0.11	7.58 ± 0.13	4.41 ± 0.52

DISCUSSION

A direct comparison between the activation parameters for ring inversion of the bridged naphthalenes and of the corresponding negative radicals cannot be made because of the lack of experimental data on the neutral molecules. However we can attempt to estimate the potential energy barriers on the parent compounds of the radicals examined by using empirical field force calculations. Calculations of this kind give answers which are usually in quite good agreement with experiment;[18,19] we therefore hopefully believe that the calculated barriers to ring inversion are reliable enough not to render completely meaningless a comparison with experimental barriers determined for the radical anions.

The conformational inversion in *peri*-bridged naphthalenes involves interconversion between two equivalent states (A) and (A′) *via* the planar transition state (B), as depicted in Scheme 1. The energies of both states (A) and (B) were calculated by assuming a fixed conformation of the aromatic rings of naphthalene.[20] Atoms of the aliphatic chain were assigned full freedom



SCHEME 1

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[15] T. C. Christidis and F. W. Heineken, *Chemical Physics*, 1973, **2**, 239; K. Ishizu, K. Mukai, H. Hasegawa, K. Kubo, H. Nishiguchi, and Y. Deguchi, *Bull. Chem. Soc. Japan*, 1969, **42**, 2808; K. Ishizu, *ibid.*, 1964, **37**, 1093.

[16] G. Binsch, *Mol. Phys.*, 1968, **15**, 469.

[17] M. Guerra, G. F. Pedulli, and M. Tiecco, *J.C.S. Perkin II*, 1973, 903.

[18] N. L. Allinger M. T. Tribble, M. A. Miller, and D. W. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1637; N. L. Allinger and J. T. Sprague, *ibid.*, 1972, **94**, 5734.

[19] J. D. Andose and K. Mislow, *J. Amer. Chem. Soc.*, 1974, **96**, 2168.

[20] O. Specchia and G. Papa, *Nuovo Cimento*, 1941, **18**, 102.

of movement. The steric energy of a particular conformation was evaluated using the potential function (1).

$$E_{\text{steric}} = \Sigma E_{\text{stretch}} + \Sigma E_{\text{bend}} + \Sigma E_{\text{twist}} + \Sigma E_{\text{nonbonded}} + \Sigma E_{\text{stretch-bend}} + \Sigma E_{\text{out of plane}} \qquad (1)$$

The force field parameters employed for 2,3-dihydronaphthalene were those tabulated by Andose and Mislow[19] which permit the treatment of both aliphatic and aromatic hydrocarbons. To calculate the energies of the pyran (II) we have adopted the additional parameters collected in Table 3. The bending parameters have been scaled to conform with the similar ones employed for hydrocarbons.[18,19] The minimization procedure used to optimize the energy of a given conformation was the 'steepest descent' method described by Schleyer and his co-workers.[21]

TABLE 3

Empirical force field parameters [a]

Stretch		k_r	r_0	
C_{sp^3}–O		5.04 [b]	1.406 [d]	
Bend		k_ψ	ψ_0	
H–C_{sp^3}–O		0.39 [c]	109.5 [d]	
C–C_{sp^3}–O		0.55 [c]	109.5 [d]	
C_{sp^3}–O–C_{sp^3}		1.30 [c]	108.5 [d]	
Twist	V_0	B	n	ϕ_{max}
C–C_{sp^3}–O–C	0.9 [e]	1.0	3	60
H–C_{sp^3}–O–C	0.9 [e]	1.0	3	60
Non-bonded		ε_{00}	$\frac{1}{2}d_{00}$	
O		0.07 [f]	1.54 [f]	

[a] For units see ref. 19. [b] H. Wieser, W. G. Laidlaw, P. J. Krueger, and H. Fuhrer, *Spectrochim. Acta*, 1968, **24A**, 1055. [c] Values scaled from those given in note *b* to account for the nonbonded 1,4-interactions as suggested by Allinger *et al.*[18] [d] Values optimized to reproduce the geometry of the dimethyl ether determined by electron diffraction, K. Kimura and M. Kubo, *J. Chem. Phys.*, 1959, **30**, 151. [e] Values reproducing the torsional barrier of the dimethyl ether reported by P. H. Kasey and R. J. Myers, *J. Chem. Phys.*, 1959, **30**, 1096. [f] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, 1969, **91**, 337.

TABLE 4

Calculated steric energies (kcal mol^{-1}) for the ground and transition states to ring inversion of 2,3-dihydrophenalene (I) and 1*H*,3*H*-naphtho[1,8-*cd*]pyran (II)

Compound	$E_{\text{ground state}}$	$E_{\text{transition state}}$	ΔE
(I)	7.15	14.31	7.16
(II)	5.01	9.92	4.91

The results of the calculations for (I) and (II) are shown in Table 4. From the minimum energy conformation of the ground state we also determined the dihedral angle between the plane containing the C–X–C atoms and the naphthalene plane, which is 47 and 43° for (I) and (II) respectively. An indication on the quality of these calculations is given by comparison of the conformations of the protons attached to the β-carbon obtained by optimizing the steric energy of the ground state with that computed from the experimental splittings measured in the slow exchange region through equation (2) where

$$a^{\text{H}} = \rho_\alpha^{\pi}(B_0 + B_2 \cos^2\psi) \qquad (2)$$

B_0 and B_2 are empirical constants, ρ_α^{π} is the spin density at the α-carbon, and ψ the dihedral angle between the plane defined by the C_α–C_β bond and the symmetry axis of the $2p_z$ orbital centred on C_α, and the plane passing through C_α, C_β, and H. As $B_0 \ll B_2$ we may write the ratio between a_{ax} and a_{eq} as in equation (3). This

$$a_{ax}/a_{eq} = \cos^2\psi_{ax}/\cos^2(\psi_{ax} + 120) \qquad (3)$$

equation gives ψ_{ax} 0.3 and 4.4°, and ψ_{eq} 120.3 and 124.4° for (I) and (II) respectively. The values of these angles are in good agreement with those computed by force field calculations, *i.e.* ψ_{ax} 1.7 and 6.7° and ψ_{eq} 121.2 and 126.5°, and give us more confidence in the quality of the force field employed.

Examination of the data of Tables 2 and 4 shows that the calculated potential energy barriers to ring inversion for compounds (I) and (II) compare favourably with the experimental activation enthalpies determined for the corresponding radical anions. This constitutes evidence that, in *peri*-bridged naphthalenes, the addition of an extra electron to the π-system has a very small effect on the height of this barrier. This behaviour is not unexpected from consideration of the individual terms contributing to the energies of the ground and transition states in the molecule and its anion radical. Actually none of these should be significantly modified by a change in the π-orbital occupation of the naphthalene group, since direct conjugation of the aromatic ring with the substituent is not possible in the present case. A non-negligible contribution might possibly arise by variation of the structure of the naphthalene ring and therefore of the distance between the carbons bridged by the aliphatic chain, which may be induced by a change in conjugation due to the presence of the additional electron. Unfortunately no experimental determination of the structure of the naphthalene negative ion has been reported, to the best of our knowledge; however, if proportionality between bond distances and bond orders is admitted, this variation, if any, should be extremely small since the p_{19} bond order is identical in naphthalene and in its anion radical.

The situation for the dibenzocycloheptene (IV) and its negative radical is completely different. Although the activation energy for ring inversion has not yet been measured for this compound, there are several indications that the potential energy barrier of 13 kcal mol^{-1} calculated by Mislow[9] should approximate reasonably well to the experimental value. If an activation energy between 13 and 14 kcal mol^{-1} is assumed for (IV) the same quantity measured for the corresponding anion radical (8.07 kcal mol^{-1}) shows a decrease of *ca.* 5—6 kcal mol^{-1}. To understand the origin of this effect we should consider the factors determining the height of the energy barrier.

Conformational inversion of the dibenzocycloheptene (IV) occurs *via* the transition state (IVB) (see Scheme 2); the potential energy difference between the states (IVA or A′) and (IVB) results from two main contributions, the steric energy which is a composite of terms arising

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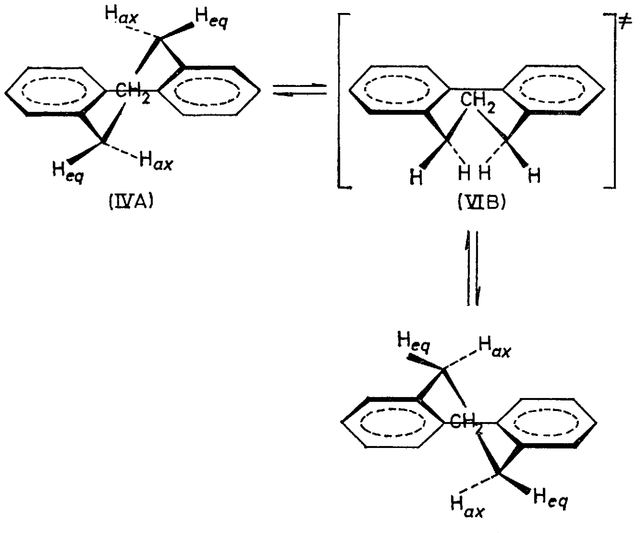
[21] J. E. Williams, P. J. Stang, and P. V. R. Schleyer, *Ann. Rev. Phys. Chem.*, 1968, **19**, 531.

from bond stretching, valence angle bending, torsional and nonbonded interactions, and the resonance energy which depends on the dihedral angle between the planes of the phenyl rings. To a first approximation the steric energy should remain practically constant on going from the neutral to the negative form of the dibenzocycloheptene. On the other hand, the addition of an unpaired electron causes, for diaryl derivatives, large variations of the conjugation along the interannular bond.[2] We can then explain the different heights of the inversion barrier only in terms of π-electron delocalization energy.



Scheme 2

An estimate of the variation of the resonance energy may be made by comparing potential energy curves calculated for the biphenyl molecule and for the corresponding anion radical, on the assumption that the steric energy is the same in both cases. Among the various calculations reported for biphenyl [22-25] we chose those of Simonetta and his co-workers since a recent n.m.r. investigation in oriented solvents of 4,4′-dichlorobiphenyl [26] showed that potential parameters similar to those given in ref. 25 provide a good fit of the experimental data. INDO Calculations were employed to compute the potential energy curve as a function of the twist angle in the case of the negative ion of biphenyl since they were found to predict reasonably well the magnitude of rotational barriers in flexible radical anions.[1,2]

The calculations were done by assuming the geometry of benzene for the phenyl rings and optimizing the energy as a function of the interannular bond distance for given values of the twist angle ψ. From the computed energy curve plotted in Figure 3 together with that for the biphenyl molecule,[25] our calculations predict in the radical anion, increased planarity of the equilibrium conformation (ψ 10°) accompanied by a reduction of the energy barrier to rotation *via* the planar transition state [$E(0°) - E(10°) = 0.19$ kcal mol^{-1}]. On the other hand rotation *via* the perpendicular transition state (ψ 90°) becomes much more difficult in energetic terms [$E(90°) - E(10°) = 31.12$ kcal mol^{-1}]. The 1,1′-bond distance was calculated to be 1.45 Å in the minimum energy conformation as opposed to the value of 1.489 Å found experimentally for biphenyl in the gas phase.[27] The drastic change in the potential energy profile on going to the radical anion may be justified in terms of the occupation by the unpaired electron of the lowest unoccupied molecular orbital of biphenyl, which has strong bonding character in the interannular region. The increased conjugation between the two rings induces stabilization of the conformation which does not deviate too much from planarity and therefore a flattening of the radical, a shortening of the 1,1′-bond, and a more pronounced slope of the energy curve for large values of the angle ψ.

Now we are able to estimate the additional amount of resonance energy which is gained by the radical anion of the dibenzocycloheptene for ψ 0°, if we know the torsional angle between the two rings in the ground state conformation. This has been calculated to be 50.6° by Mislow *et al.*[9] Assuming the same steric energy for radical and parent compound, the energy difference between the inversion barrier in the two systems is

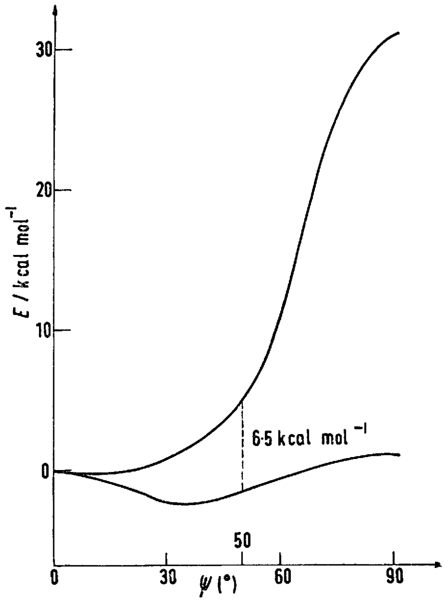


Figure 3 Potential energies for biphenyl (lower curve) and its radical anion (upper curve) as a function of the twist angle ψ

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[22] F. J. Adrian, *J. Chem. Phys.*, 1958, **28**, 608.

[23] I. Fischer-Hjalmars, *Tetrahedron*, 1963, **19**, 1805.

[24] M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc.*, 1970, *A*, **315**, 443.

[25] G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Mol. Phys.*, 1968, **15**, 339.

[26] W. Niederberger, P. Diehl, and L. Lunazzi, *Mol. Phys.*, 1973, **26**, 571.

[27] O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1949, **4**, 926.

equal to the separation between the potential energies calculated for biphenyl and its anion radical at the torsion angle of the dibenzocycloheptene. As Figure 3 shows this value is 6.5 kcal mol^{-1}, which is in good agreement with the difference of 5—6 kcal mol^{-1} previously estimated.

We conclude that in radical anions of conjugated derivatives the energy barriers to ring inversion may differ considerably from those of the parent compounds whenever ground and transition states accommodate different amounts of π-delocalization energy. On the other hand, in systems such as bridged naphthalenes where no variation of resonance energy is involved during inversion, the height of the barrier should be much the same for the neutral and radical forms. Exceptions may result when a pronounced reorganization of solvent molecules occurs on going from the ground to the transition state;[4] however this situation is usually revealed by large deviations of the activation entropy from zero, which should be expected for ring inversions.

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