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2-(*p*-Dimethylaminophenyl)indan-1,3-dione-2-yl Radical: ENDOR and ESR Studies and MNDO Calculation

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ENDOR and ESR spectra of the 2-(*p*-dimethylaminophyenyl)indan-1-,3-dione-2-yl radical were measured in toluene and diethyl phthalate at 350 K. A solvent dependence of the coupling constants was observed. Using the MNDO method, the optimized structure of the radical and the spin population distribution were derived.

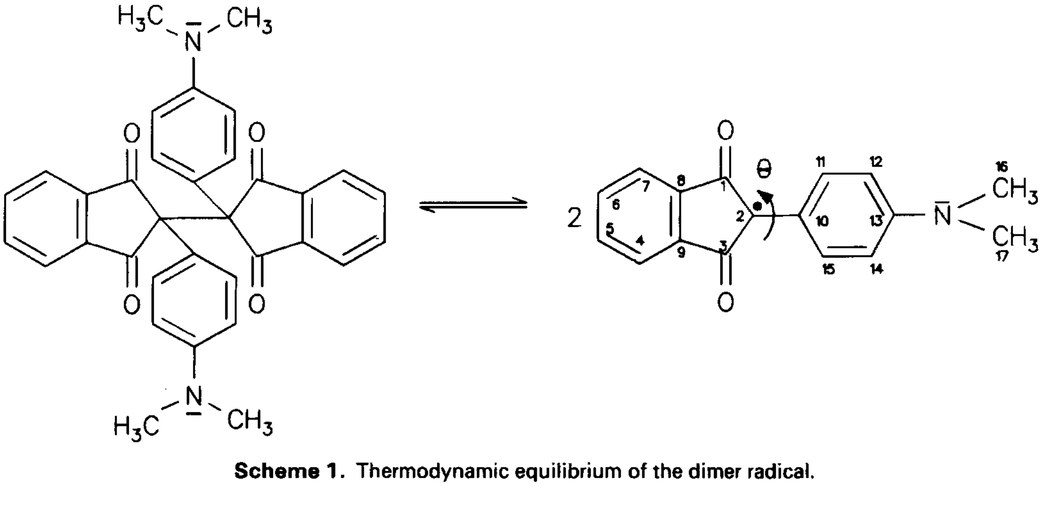
KEY WORDS ESR; ENDOR; 2-Arylindan-1,3-dione-2-yl radical

INTRODUCTION

Aromatic 2-arylindan-1,3-dione-2-yl radicals are intermediates in the inhibited liquid-phase oxidation of alkyl-aromatic hydrocarbons.[1] In liquid solution the radicals exist in equilibrium with their dimers (Scheme 1). Consequently, a permanent concentration of radicals can be observed. Moreover, the capability of the radicals to undergo bimolecular self-reaction in liquid,[2] their persistence in the presence of other agents (including solvents) and the variety of the derivatives available from them allow convenient investigation of the correlations between the structure and reactivity of the radicals. Besides forming via homolytic cleavage of the dimer, the radicals studied can also be obtained via decomposition of 2-(*p*-dimethylaminophenyl) indan-1,3-dione by formal loss of a hydrogen atom.[3]

EXPERIMENTAL

2,2′ - Bis[2 - (dimethylaminophenyl)indan - 1,3 - dione] dimer was obtained using the procedure described earlier.[3] The studied samples were carefully deoxygenated by bubbling nitrogen through the solutions used. The ESR spectra were recorded on either a Varian



Scheme 1. Thermodynamic equilibrium of the dimer radical.

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E-12 or a Bruker ESR-300 spectrometer. A Varian E-line-Century ESR spectrometer equipped with a Bruker ER 810 ENDOR unit and a Bruker ER 140 data system were used for the ENDOR experiments. The instrumental spectroscopic parameters were adjusted in each case in order to obtain complete spectral resolution and a reasonable signal-to-noise ratio.

The molecular orbital calculations were carried out with the MNDO (Modified of Diatomic Overlap) method[4] without inclusion of configuration. The molecular structure of the radical was optimized by use of the David–Fletcher–Powell algorithm. The spin population was determined from the square of the coefficient of the atomic orbitals.

RESULTS AND DISCUSSION

2-(*p*-Dimethylaminophenyl)indan-1,3-dione-2-yl radical was produced by homolytic thermal cleavage of 2,2′-bis[2-(*p*-dimethylaminophenyl)indan-1,3-dione] dimer, in toluene or in diethyl phthalate. Owing to this equilibrium, the intensity of the ESR and ENDOR spectra increases with increase in temperature.

Figure 1 shows the well resolved ESR spectrum of the radical observed in diethyl phthalate. The complex hyperfine structure suggests extensive delocalization of the single unpaired electron. The proton coupling constants obtained from ENDOR experiments are presented in Table 1. Using these data and spectrum simulation, a refinement of the values and determination of the number of the coupling nuclei and of the splitting constant of the nitrogen were achieved. The ESR data obtained by this procedure are included in Table 1.

The assignment of the splitting constants to the methyl protons and the nitrogen is unequivocal, but the attribution of the other coupling constants was made by comparison with analogous aromatic radicals[5–7] and by spin population calculation.

The ESR and ENDOR spectra of the same radical in toluene at 350 K are given in Figs 2 and 3. The analysis

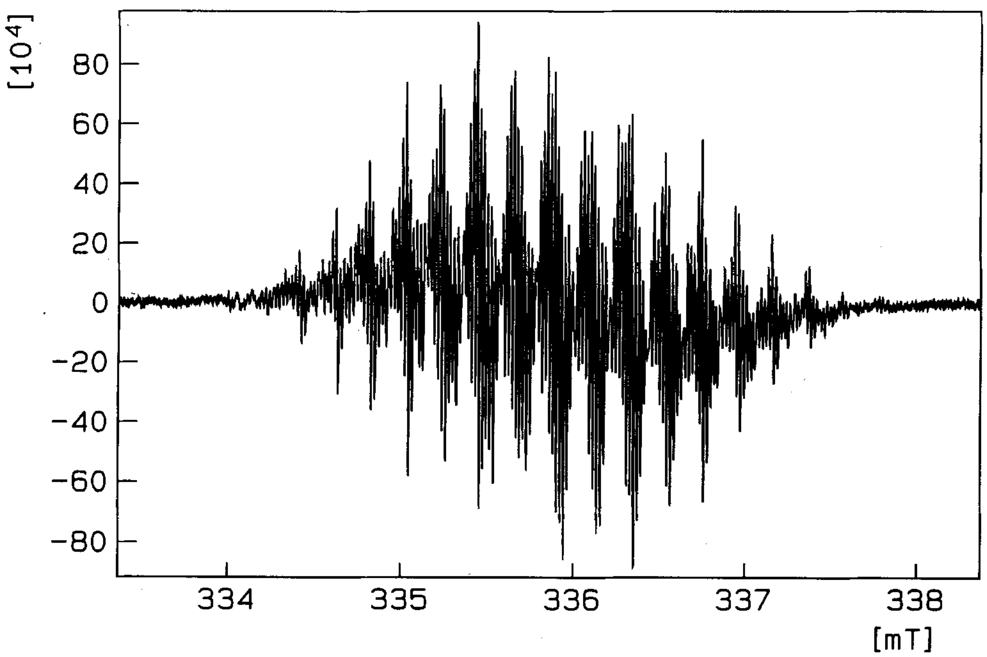


Figure 1. ESR spectrum of the 2-(*p*-dimethylaminophenyl)indan-1,3-dione-2-yl radical produced in diethyl phthalate at 350 K.

Table 1. Hyperfine coupling constants obtained from the experimental ENDOR and simulated ESR spectra of the 2-(*p*-dimethylaminophenyl)indan-1,3-dione-2-yl radical generated in diethyl phthalate and toluene

		Hyperfine coupling constants (mT)					
Solvent	Method	$a^H_{4,7}$	$a^H_{5,6}$	$a^H_{11,15}$	$a^H_{12,14}$	a^N	a^{CH3}
Diethyl phthalate	ENDOR	0.02	0.04	0.21	0.08	0.50	0.41
	ESR	0.02	0.05	0.21	0.08	0.50	0.41
Toluene	ENDOR	0.02	0.05	0.27	0.05	0.40	0.36
	ESR	0.02	0.04	0.25	0.04	0.39	0.34

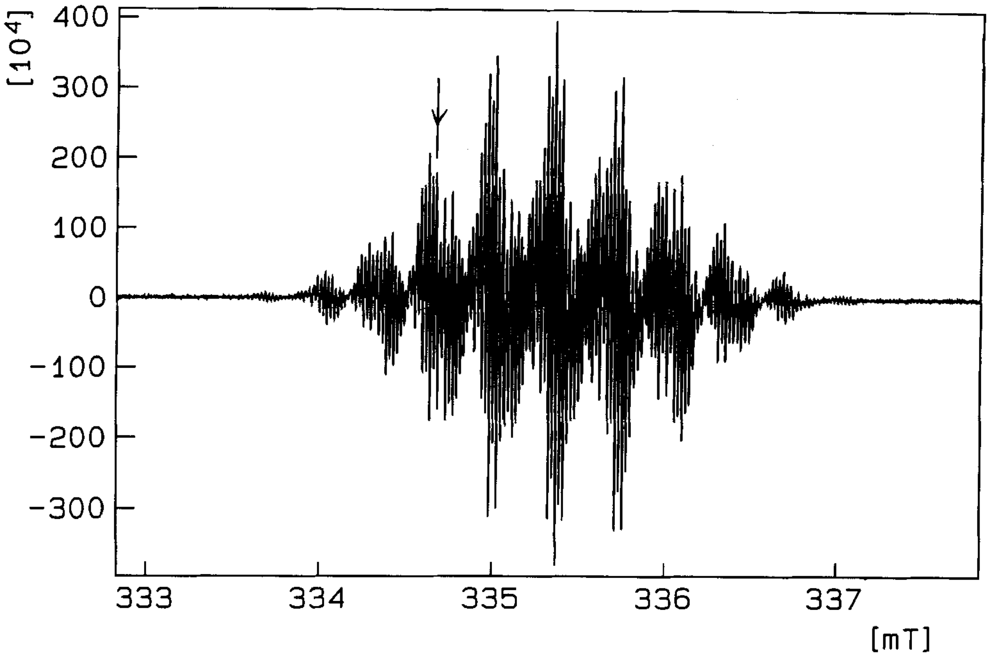


Figure 2. ESR spectrum of the radical produced in toluene at 350 K. The arrow indicates the field setting for the ENDOR experiment.

of this ESR spectrum could be carried out with the help of ENDOR experiments and spectrum simulation, as outlined above. The data obtained are presented in Table 1.

Table 2 compares the calculated structure of the radical with the experimental structure of its dimer[8] and of the corresponding enol molecule of 2-(*p*-dimethylaminophenyl)-1,3-indandione.[9]

The most striking result of the calculation is that the C-1,-2, -3 and -10 atoms are in the same plane (the deviation from plane is 0.3°). This implies that C-2 (Scheme 1) has sp^2 hybridization and the structure of the radical is similar to that of the enol molecule. The agreement between the calculated bond distances and angles for the radical phthaloyl fragment and the corresponding parameters for the enol molecule, as determined from x-ray diffraction,[9] is generally satisfactory (see Table 2). The most significant differences are observed for the dimethylaminophenyl fragment. The plane of the phenyl ring forms the torsion angle $\theta = 28.8°$ with the plane of the indan ring. The value of this angle is determined by the balance between steric and electronic interactions within the radical. For comparison, the analogous angle between phenyl rings is about 30° in biphenyl.[10] The C-2—C-10 bond length (1.412 Å) is significantly shorter than the corresponding distance in the dimer (1.52 Å) and in the enol molecule (1.49 Å). Another peculiarity of the calculated radical structure is that the N—C-13 bond length (1.398 Å) is characteristic of nitrogen atoms, conjugated with the aromatic systems. Thus, the resonance forms shown in Scheme 2 are believed to contribute significantly to the radical structure.

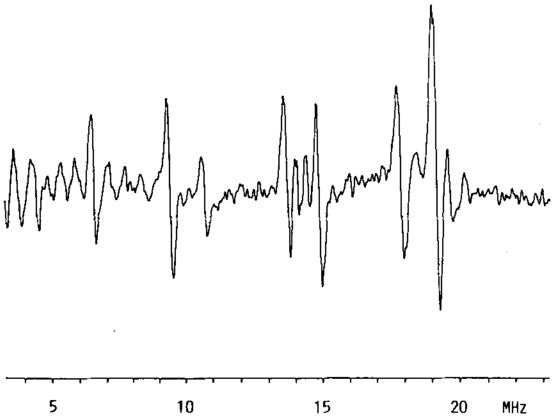


Figure 3. ENDOR spectrum of the radical produced in toluene at 350 K.

The spin population distribution is shown in Scheme 3. A high spin population (53%) appears on the dimethylaminophenyl fragment of the radical, while about 36% residues on the reactivity centre (C-2) and only 11% exist on the phythaloyl fragment. The spin population at the *ortho* position of the phenyl ring is larger than that at the *meta* position. This confirms the assignment of coupling constants of 0.214 and 0.079 mT to the *ortho* and *meta* positions, respectively (Table 1). The splittings of 0.044 and 0.018 mT are believed to be coupling constants of the protons at positions 5,6 and 4,7 (Scheme 1), respectively. A similar correlation between these coupling constants (the proton coupling constant at position 5,6 is larger than that at 4,7) was obtained for the radical anion of 2-phenyl indan-1,3-dione.[7] It should be noted that the spin population was derived without inclusion of configuration interaction, and for this reason no spin population was obtained on methyl groups. Inclusion of electron correlation will undoubtedly give a more precise spin-population

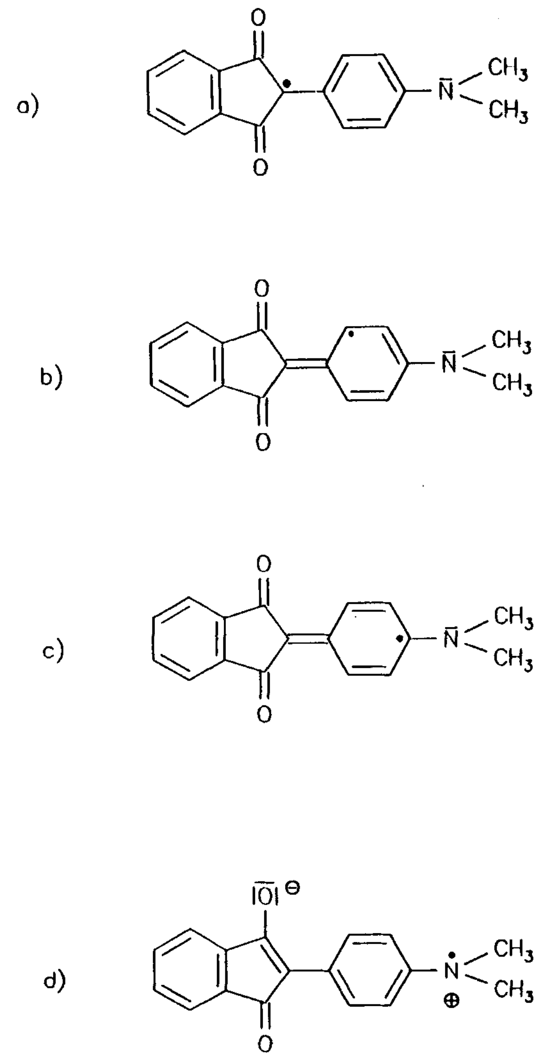
Table 2. **Calculated and experimental structures of the 2-(*p*-dimethylaminophenyl)indan-1,3-dione-2-yl radical, corresponding dimer and enol molecule**

Parameter	Calculated radical	x-ray, enol[12]	x-ray, dimer[11] [b]
C=O	1.228	1.250	1.193, 1.210
C1—C2, C2—C3	1.496	1.450	1.524, 1.564
C1—C8, C3—C9	1.503	1.500	1.460, 1.477
C8—C7	1.395	1.385	1.384, 1.394
C7—C6	1.416	1.400	1.365, 1.387
C6—C5	1.402	1.390	1.382, 1.384
C5—C4	1.418	1.390	1.373, 1.377
C2—C10	1.412	1.457	1.522, 1.526
C10—C11, C10—C15	1.445	1.390	1.378, 1.389
C11—C12	1.389	1.390	1.371, 1.375
C12—C13	1.436	1.410	1.382, 1.389
C13—N	1.398	1.400	1.380, 1.384
N—C16, N—C17	1.468	1.460	1.459, 1.466
C13—C14	1.436	1.370	1.389, 1.395
C14—C15	1.389	1.400	1.364, 1.376
C1—C2—C3	106.8	105.8	101.1, 101.7
C1—C2—C10	126.8	128.3	106.9, 107.8
O—C1—C2	127.9	128.6	124.1, 127.0
C9—C3—C2	107.8	108.8	106.3, 107.8
O—C1—C8	124.8	122.9	126.0, 126.3
C1—C8—C7	131.0	132.0	127.8, 129.8
C1—C8—C9	109.4	107.4	111.3, 111.4
C8—C7—C6	118.4	117.0	116.7, 119.3
C7—C6—C5	120.9	121.3	121.3, 121.6
C6—C5—C4	120.7	120.2	120.2, 121.8
C5—C4—C9	118.7	119.3	117.5, 118.5
C7—C8—C9	121.0	121.5	119.1, 120.9
C2—C10—C11	123.1	122.3	121.7, 122.3
C11—C10—C15	113.7	115.8	115.7, 116.8
C10—C11—C12	123.4	122.0	121.0, 122.5
C11—C12—C13	122.5	121.5	121.1, 122.1
C12—C13—C14	114.7	116.5	117.1, 116.8
C14—C15—C10	122.9	122.3	122.9, 122.1
C12—C13—N	122.7	122.8	122.5, 121.7
C13—N—C16	121.1	121.7	119.9, 120.9
C16—N—C17	117.9	119.4	117.8, 118.5

[a] Bond lengths are given in Å and angles in degrees. Numeration of atoms is shown in scheme 1.

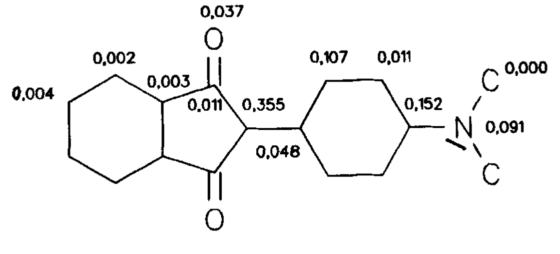
[b] Parameters of two 2-(*p*-dimethylaminophenyl)indan-1,3-dione-2-yl fragments.

picture. In this paper we mainly pay attention to the optimized structure of the radical. The solvent effect for this radical was discussed by Khudyakov *et al.*[11]



Scheme 2. Main resonance forms of the 2-(*p*-dimethylaminophenyl)indan-1,3-dione-2-yl radical.

In the radical crystal structure the phenyl ring forms an angle $\theta = 28.8°$ with the plane of the indan ring. The value of this angle was derived in the solid phase without taking into account the interaction between the radical molecule and the surrounding solvent molecules. It has been shown[12,13] that the interaction between the solvent molecules and radical molecules influences the polar resonance structure and changes the radical conformation, in particular the torsion angle. For comparison, the analogous angle θ is about 15° in the enol molecule, which is solvated by polar molecules.[9] The decrease in θ results in an increase in the spin population residing on the dimethylaminophenyl fragment of the radical. It may be expected that the resonance forms shown in Scheme 2c and d may be more important for radicals in polar solvents. That means an increase in the nitrogen and methyl proton coupling constants; this is in agreement with the experiment (Table 1). These resonance forms imply a decrease also in radical reactivity in bimolecular self-reactions. In fact, the equilibrium constant of the dimer radical is increased in polar solvents.[2,14] Hence, we suggest that the experimental variation between the values of the radical coupling constants in different solvents is due to specific solvation.



Scheme 3. Unpaired electron spin population distribution.

In summary, ENDOR and ESR spectra of the 2-(*p*-dimethylaminophenyl)indan-1,3-dione-2-yl free radical were obtained at 350 K in toluene and diethyl phthalate. The differences in these spectra are mainly due to the variation of the coupling constants attributed to the dimethylamino fragment. Using MNDO calculations, the optimized structure and spin population were determined. The observed experimental differences in the coupling constants are attributed to specific solvation effects.

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