ESR and ENDOR Study on the Radical Ions of Two Non-Alternant Hydrocarbons: 1,3,5,7-Tetra-tert-butyl-s-indacene and 2,7-Di-tert-butylidicyclopenta[a,e]cyclooctene

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The radical anions and radical cations of two alkyl-substituted non-alternant hydrocarbons, 1,3,5,7-tetra-tert-butyl-s-indacene and 2,7-di-tert-butyldicyclopenta[a,e]cyclooctene, were characterized by their proton coupling constants with the use of ESR and, in part, ENDOR spectroscopy. Considering the unusual electronic structures of the π-systems in question, these values agree fairly well with those predicted by simple MO theory. Also reported are the proton hyperfine data for the radical ions of the likewise alkyl-substituted non-alternant 8,16-diisopropyl-s-indacenod[1,2,3-cd:5,6,7-c'd']diphenalene

KEY WORDS ESR; ENDOR; radical anions; radical cations; s-indacene; dicyclopenta[a,e]cyclooctene; s-indaceno[1,2,3-cd:5,6,7-c'd']diphenalene

INTRODUCTION

The non-alternant hydrocarbons s-indacene (1) and dicyclopenta[a,e]cyclooctene (3) can be regarded as annulenes which are cross-linked by two single bonds. For 1, a formal derivative of the 'antiaromatic' [12]annulene, several workers initially predicted a ground state of $C_{2v}$ symmetry, 1A, or its valence isomer, 1B, with localized double bonds.1-3 However, this prediction has not been directly verified by experiment, because no structural data are available for this unstable and highly reactive compound.4 On the other hand, 1,3,5,7-tetra-tert-butyl-s-indacene (2), synthesized several years ago,1 is stable and has been thoroughly studied. The π-system of 2 exhibits an effective $D_{2h}$ symmetry, both in crystals1,3 and in solution down to 143 K,4 a finding which points to a ground state 2C or to a very low barrier for interconversion 2A ⇄ 2B. Furthermore, high-level ab initio calculations, recently performed on 1,6 indicate that even the parent compound prefers 1C over 1A or 1B. An analogous statement should hold also for (the still unknown) dicyclopenta[a,e]cyclooctene (3), a formal derivative of the 'aromatic' [14]annulene; a ground state 3C of $D_{2h}$ symmetry is expected to be energetically favoured over its $C_{2v}$ counterparts, 3A or 3B, with localized double bonds. This expectation has been borne out by experimental findings for 2,7-di-tert-butyldicyclopenta[a,e]cyclooctene (4), also synthesized a few years ago.7 The $D_{2h}$ symmetry observed for the π-system of 4 in crystals and in solution7 is again consistent with 4C rather than with the less symmetric 4A or 4B. It is noteworthy that this system embraces a fully planar eight-membered ring which is rarely found in compounds containing the cyclooctatetraene moiety.8,9

Here, we report on the radical anions and the radical cations of 2 and 4 which have been characterized by their hyperfine data with the use of ESR and, in part,
ENDOR spectroscopy. The finding that these data reflect the $D_{3h}$ symmetry of the π-systems is not surprising, because radical ions generally have more propensity to π-electron delocalization than their neutral precursors. Therefore, 2'−, 2''−, 4'− and 4''− will throughout be considered as 2C'−, 2C'', 4C'− and 4C'', without an explicit specification by the symbol C.

RESULTS AND DISCUSSION

MO models

Figure 1 and 2 depict diagrammatically the frontier orbitals of s-indacene (1) and dicyclopenta[a,e]cyclooctene (3) as emerging from the Huëckel MO model. The lowest unoccupied orbital (LUMO) of 1, $\psi_1(b_{3g})$, is non-bonding $(E_a = \alpha)$, whereas the highest occupied orbitals (HOMOs) of 1, $\psi_5(b_{2g})$ and $\psi_6(a_u)$, are strongly bonding and degenerate $(E_a = E_b = \alpha + 0.62\beta)$ (this degeneracy is traced back to that of the bonding cyclopentadienyl orbitals which are pairwise contained in $\psi_1$ and $\psi_2$). Upon 1,3,5,7-tetra-tert-butyl substitution of 1, to yield 2, the energies $E_j$ $(j = 5, 6$ and $7)$ are raised by the first-order inductive perturbation $\Delta E_j = \sum c_{j\mu}^2 d_{\mu a}$, where $c_{j\mu}$ is the LCAO coefficient for $\psi_j$ at the substituted π-centre $\mu$ $(= 1, 3, 5$ and $7)$ and $d_{\mu a}$ is the change in the parameter $a$, at this centre.$^{10}$ With $d_{a2} = -0.3\beta$, $E_6 = 0.09\beta$, $E_5 = -0.22\beta$, $E_4 = \alpha + 0.13\beta$, $E_3 = \alpha + 0.60\beta$. The degeneracy of $\psi_1$ and $\psi_2$ is thus removed and the latter orbital becomes the HOMO of 2 (Fig. 1).

The LUMO of dicyclopenta[a,e]cyclooctene (3), $\psi_6(b_{2u})$, is also non-bonding $(E_b = \alpha)$, while the HOMO of 3, $\psi_4(b_{1u})$, is moderately bonding $(E_a = \alpha + 0.35\beta)$. 2,7-Di-tert-butyl substitution of 3, to yield 4, affects these frontier orbitals less than those of 1 on passing to 2. Thus, the first-order inductive perturbation $\Delta E_j = \sum c_{j\mu}^2 d_{\mu a}$, where $j = 7$ and $8$, $\mu = 2$ and $7$ and $d_{2a} = -0.3\beta$, raises the energies by $2(-0.3\beta)c_{j\mu}$ to give $E_j = \alpha - 0.10\beta$ and to leave $E_7$ unaffected in this approximation (Fig. 2).

The MO models predict that, despite the tert-butyl substitution, compounds 2 and 4 should be easily reduced to their radical anions 2'− and 4'−, whereas oxidation of 2 and 4 to the corresponding radical cations, 2'^+ and 4'^+, may proceed less readily.

Table 1 lists the π-spin populations $\rho_\pi$ in the radical ions of 2 and 4 calculated by the McLachlan modification of the Huëckel MO model $(i = 1.2).^{11}$ Using the McConnell equation,$^{12}$ $a_\pi(\mu) = Q \rho_\pi$, with $Q = -2.2$ mT for radical anions and $-2.6$ mT for radical cations,$^{13}$ the following predictions can be made for the coupling constant $a_\pi(\mu)$ of the protons attached to π-centres $\mu$ (π-protons).

<table>
<thead>
<tr>
<th>Position $\mu$</th>
<th>1, 3, 5, 7</th>
<th>2, 6</th>
<th>4, 8</th>
<th>3a, 4a, 7a, 8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2''^-$</td>
<td>+0.23</td>
<td>-0.07</td>
<td>+0.20</td>
<td>-0.05</td>
</tr>
<tr>
<td>$2'^-$</td>
<td>+0.22</td>
<td>-0.06</td>
<td>+0.05</td>
<td>+0.08</td>
</tr>
<tr>
<td>$4''^-$</td>
<td>-0.04</td>
<td>-0.13</td>
<td>+0.10</td>
<td>+0.12</td>
</tr>
<tr>
<td>$4'^-$</td>
<td>+0.26</td>
<td>+0.06</td>
<td>+0.05</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

The predictions for the tert-butyl π-protons are less reliable, because of the small magnitude of their coupling constants. Splittings from such protons should be

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Table 1. π-Spin populations, $\rho_\pi$, predicted by the McLachlan procedure for the radical ions of 2 and 4.
observable in ESR spectra of $2^-$, $2^+$, and $4^-$ but not in that of $4^+$. Radical anions

Cyclic voltammograms of 2 and 4 indicated that both compounds undergo irreversible reduction to their radical anions, $2^-$ and $4^-$, at potentials which are substantially less negative than those of most hydrocarbons, $-0.81 \pm 0.02$ and $-1.00 \pm 0.02$ V vs. SCE, respectively. For spectroscopic studies, $2^-$ and $4^-$ were generated from 2 and 4 by reaction with potassium in 1,2-dimethoxyethane (DME). They were relatively persistent and gave rise to well resolved ESR and ENDOR spectra as shown in Figs 3 and 4. These spectra, taken in the range 203–298 K, depended slightly on the temperature.

The ESR hyperfine pattern of $2^-$ (Fig. 3) is a triplet spaced by $0.395 \pm 0.002$ mT and split into another triplet by $0.109 \pm 0.001$ mT. Both coupling constants, $a_H(\mu)$, each of two $\alpha$-protons responsible for this pattern, were also determined from the pairs of corresponding ENDOR signals (Fig. 3). In addition, the ENDOR spectrum of $2^-$ exhibited a third pair of signals close to the free proton frequency $v_H$. The coupling constant associ-
0.196 ± 0.002 mT, while the splitting within each component of the quintet arises from another set of four α-protons and the 18 tert-butyl γ-protons having values of 0.038 ± 0.001 and 0.017 ± 0.001 mT, respectively. Each of the three sets of protons gave rise to a pair of ENDOR signals associated with its coupling constant (Fig. 4). Again, a general-TRIPLE-resonance experiment indicated that the largest value, 0.196 mT, has a sign opposite to that of the two smaller ones, 0.038 and 0.017 mT. Assignments of 0.196 mT, with a negative sign, to \( \mu = 4, 5, 9, 10 \) and of 0.038 mT, with a positive sign, to \( \mu = 1, 3, 6, 8 \) are consistent with the MO model. The \( _{13} \text{C} \) satellite lines in the ESR spectrum of 4' (Fig. 4) were not analysed in detail. The pertinent \( _{13} \text{C} \) coupling constants \( \alpha_{c}(\mu) \) lie in the range 0.4–0.5 mT and are compatible with the values calculated for the carbon sites \( \mu = 1, 3, 6, 8 \) and 2, 7, the former being negative and the latter positive.

**Radical cations**

Oxidation of 2 and 4 to their radical cations, \( 2^{+} \) and \( 4^{+} \), proved more problematic than their reduction to the corresponding radical anions, \( 2^{-} \) and \( 4^{-} \). The cyclic voltammogram of 4 exhibited an irreversible oxidation wave at +0.51 V vs SCE, whereas for 2 no wave was discerned up to +0.8 V. Both radical cations \( 2^{+} \) and \( 4^{+} \) had a low persistence and could be generated for spectroscopic studies only under special conditions.

In the case of \( 2^{+} \), ESR and ENDOR spectra were observed on oxidation of 2 with tris(p-bromophenyl) ammonium hexachloroantimonate in dichloromethane at 200–230 K and with thallium(III) trifluoroacetate in trifluoroacetic acid at room temperature. Some of these spectra are presented in Fig. 5. The two \( \alpha \)-protons responsible for the triplet in the ESR spectrum have a coupling constant, \( \alpha_{d}(\mu) \), of 0.226 ± 0.003 mT, while the hyperfine pattern in each component of the triplet stems from an other pair of \( \alpha \)-protons with a value of 0.091 ± 0.002 and from the 36 \( \gamma \)-protons of the four tert-butyl substituents with 0.028 ± 0.001 mT. The spectra were markedly temperature dependent, owing to a hindered free rotation of the bulky tert-butyl substituents. Each of the ENDOR signals from the protons in these substituents was split into two with an intensity ratio of 2:1 and associated coupling constants of 0.036 ± 0.001 and 0.013 ± 0.001 mT, respectively; the weighted average of the two values is equal to 0.028 mT observed in the ESR spectra. Thus, the three methyl groups in a tert-butyl substituent are inequivalent on the hyperfine time-scale, one of them differing from the other two in its environment. On raising the temperature, the pertinent signals broadened but coalescence was not attained by 300 K (Fig. 5). Because of the lower resolution relative to ENDOR spectroscopy, this inequivalence did not manifest itself directly by an additional splitting of the ESR lines. Nevertheless, simulations of the ESR spectra at several temperatures revealed an exchange broadening and led to an estimate of 40 kJ mol\(^{-1}\) for the barrier to rotation of the tert-butyl substituents in \( 2^{+} \). It is noteworthy that a hindrance to such a rotation failed to be observed in the \( ^{1} \text{H} \) and \( ^{13} \text{C} \) NMR spectra of the neutral compound 2 in a broad temperature range\(^4\) or in the ESR and ENDOR spectra of the radical anion \( 2^{-} \) at 203–298 K. For \( 2^{+} \), this failure may be due to the vanishingly small magnitude of the coupling constant (0.005 mT) of the tert-butyl protons. The results of the general-TRIPLE experiment were not fully conclusive for \( 2^{+} \), as they merely pointed out that the coupling constants of 0.091, 0.036 and 0.013 mT have the same sign, whereas the relative sign of the largest value, 0.226 mT, remained undetermined. Theory requires that both coupling constants of the \( \alpha \)-protons, 0.226 and 0.091 mT, should be positive and that they have to be assigned to the positions \( \mu = 2, 6 \) and 4, 8, respectively.

The procedures used for generation of \( 2^{-} \) from 2 were unsuccessful in producing \( 4^{-} \) from 4. An ESR spectrum of \( 4^{+} \) could, however, be observed upon careful oxidation of 4 with aluminium trichloride in dichloromethane at low temperatures and subsequent
warming to 298 K. The spectrum, shown in Fig. 6, is a quintet of quintets, arising from two sets of four \( \alpha \)-protons with the coupling constants, \( a_{\alpha}(\mu) \), of 0.662 ± 0.005 and 0.108 ± 0.001 mT. The unresolved splitting from the 18 tert-butyl \( \gamma \)-protons was determined as 0.005 ± 0.001 mT from the linewidths by simulation. The observed hyperfine data are entirely consistent with theory, which assigns the larger \( a_{\alpha}(\mu) \) value of 0.662 mT to the positions \( \mu = 1, 3, 6, 8 \) and the smaller one, 0.108 mT, to \( \mu = 4, 5, 9, 10 \); both values should be negative. A negative sign is also expected for 0.005 mT, as the tert-butyl \( \gamma \)-protons are attached to centres \( \mu = 2, 7 \) of negative \( \pi \)-spin population, in contrast to 2', 2" and 4', 4" but not in those of 4'. It has been pointed out in a recent high-level \textit{ab initio} study of \( \delta \)-indacene\footnote{6} that the electron occupancy numbers of the highest bonding orbitals, \( \psi_1 \) and \( \psi_6 \), in the neutral molecule 1 are markedly lower than 2, and that such number of the lowest antibonding orbital, \( \psi_7 \), is close to 0.5. Assignment of the unpaired electron to a single orbital in the radical ions of 2 might thus not be fully adequate and lead to some discrepancies between theory and experiment. 

**EXPERIMENTAL**

Syntheses of the compounds were described previously: \(2,4'\) \textsuperscript{7} and \(6\) \textsuperscript{7} (see Appendix). The cyclic voltammograms were obtained on a Metrohm Polarecord E506 with a VA scanner E612/VA Stand 663. The following conditions were used: solvent, N,N-dimethylformamide for 2 and acetonitrile for 4; working electrode, hanging Hg drop for reduction and Pt disc for oxidation; counter-electrode, glassy carbon for reduction and Pt wire for oxidation; reference electrode, Ag/AgCl; scan, 300 mV s\textsuperscript{-1} for 2 and 100 mV s\textsuperscript{-1} for 4; room temperature. ESR spectra were taken on a Varian-E9 instrument and ENDOR and TRIPLE-resonance studies were carried out with a Bruker ESP-300 system.

**Acknowledgement**

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REFERENCES


APPENDIX

In s-indaceno[1,2-3-cd:5,6,7-c'd']diphenalen (5), the π-system of s-indacene (1) is fused to those of two phenalenyls (7). According to the Hückel MO model of 5, the LUMO ψ₁₁(BO₃) is non-bonding (E = α), whereas the HOMO ψ₁₁(a₈) is weakly bonding (E = α + 0.24β). These frontier orbitals combine the LUMO ψ₁₁(BO₃) and the HOMO ψ₁₁(a₈) of 1, respectively, with two non-bonding MOs of 7 (Fig. 8). For the recently synthesized 8,16-diisopropyl-s-indaceno[1,2-3-cd:5,6,7-c'd']diphenalen (5), only slightly perturbed (δₓ₈ = 0.3β; ΔEₓ₈ = -0.04β), while ψ₁₁(a₈) is not affected by the alkyl substitution in the first-order approximation (Fig. 8). Therefore, the MO predictions for 5 and its radical ions also hold for the corresponding species of 6. Consequently, 6 should be easily converted into both radical ions, with the pattern of the π-spin distribution in each of the two phenalenyl moieties closely resembling that in the radical 7. In the cyclic voltammogram of 6, a reversible reduction wave and an irreversible oxidation wave were already observed at ~0.48 ± 0.01 and +0.65 ± 0.01 V vs. SCE, respectively. The expected similarity of the π-spin distribution in 6⁻ and 6⁺ with that of 7⁻ was borne out by the ESR and ENDOR spectra of these radical ions.

Figure 8. Frontier orbitals of s-indaceno[1,2-3-cd:5,6,7-c'd']diphenalen (5) and the effect of 8,16-diisopropyl substitution (6) on their energies.

Table 2. Coupling constants, aₘ(μ) in mT, of the protons in the radical ions of 6, as compared with the corresponding values for the radical 7⁻.

<table>
<thead>
<tr>
<th>Species</th>
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<th>3, 5, 11, 13</th>
<th>4, 12</th>
<th>8, 16</th>
</tr>
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<tr>
<td>Position μ</td>
<td>2, 8</td>
<td>3, 7</td>
<td>4, 6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6⁻ ⁻</td>
<td>+0.091</td>
<td>-0.261</td>
<td>-0.288</td>
<td>+0.079</td>
<td>+0.023*</td>
</tr>
<tr>
<td>6⁻ ⁺</td>
<td>+0.044</td>
<td>-0.257</td>
<td>-0.287</td>
<td>+0.080</td>
<td>&lt;0.01*</td>
</tr>
<tr>
<td>7⁻ ⁻</td>
<td>-0.181</td>
<td>-0.629</td>
<td>-0.629</td>
<td>+0.181</td>
<td></td>
</tr>
</tbody>
</table>