281. Radical Ions in the Pentalene Series. Part I. 1,3,5-Tri-*t*-butylpentalene

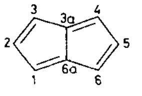
by **Peter Fürderer** and **Fabian Gerson**
Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel
and **Klaus Hafner**
Institut für Organische Chemie der Technischen Hochschule Darmstadt, Petersenstrasse 22, D-6100 Darmstadt

(29.IX.78)

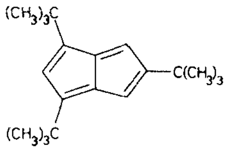
Summary

The ESR. spectra of the radical anion and cation of 1,3,5-tri-*t*-butylpentalene (II) have been reexamined under higher resolution. With the assistance of the ENDOR. technique, the coupling constants of all protons in II$^{\ominus\cdot}$ and II$^{\oplus\cdot}$ could be determined. The experimental data agree satisfactorily with the values predicted by the simple MO model which suggests that the π-spin distributions in II$^{\ominus\cdot}$ and II$^{\oplus\cdot}$ should not strongly differ from those in the corresponding radical ions of parent pentalene (I). As in the case of other non-alternant hydrocarbons, the proton coupling constants for II$^{\ominus\cdot}$ are very sensitive to experimental conditions, due to the association of the radical anion with its counterion. Spectra of II$^{\ominus\cdot}$ taken at low temperatures (down to 133 and 163 K for ESR. and ENDOR., respectively) have not revealed specific line-broadening which could arise from the bond shift between the two *Kekulé*-structures of pentalene.

Introduction. - Pentalene (I) represents a simple non-alternant 8π-electron system of considerable theoretical interest [1]. Neither the parent compound I nor its methyl derivatives could be isolated in pure form [2]. 1,3,5-Tri-*t*-butylpentalene (II) is the only alkyl derivative which proved to be stable at room temperature, when prolonged exposure to air is avoided [3]. The ESR. spectra of the radical anion II$^{\ominus\cdot}$ and the radical cation II$^{\oplus\cdot}$ have recently been observed by *Johnson* [4] who reported some of the proton coupling constants. In the present work, owing to a higher resolution of these spectra and to the use of the ENDOR. technique, a complete analysis of the hyperfine patterns has been achieved for both radical ions studied under a variety of experimental conditions.



I



II

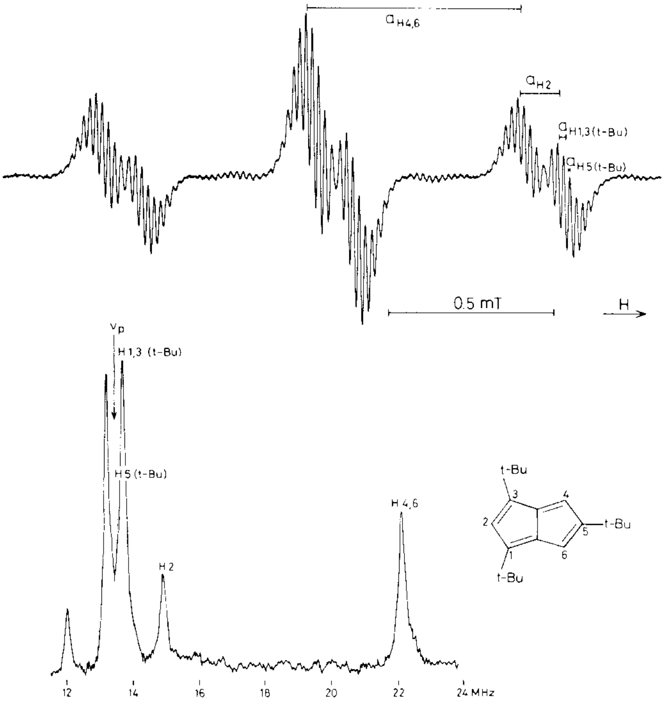


Fig. 1. *ESR. and ENDOR. spectra of the radical anion of 1,3,5-tri-*t*-butylpentalene (II).* Solvent: MTHF; counterion: $Na^{\oplus}$; temp.: 273 (ESR.) and 203 K (ENDOR.). ν_P = frequency of the free proton.

Table 1. *Proton coupling constants,* a_{H_μ}[a]) in mT, *for the radical anion of 1,3,5-tri-*t*-butylpentalene (II)*[b])

Solvent	MTHF				DME/HMPA		DMF	DMSO	CH_2Cl_2
Counterion	$Na^{\oplus}$		$K^{\oplus}$		$Na^{\oplus}$	$K^{\oplus}$	$Et_4N^{\oplus}$	$Bu_4N^{\oplus}$	$Bu_4N^{\oplus}$
Temp. (K)	213	293	213	293	213	213	213	293	193
μ = 1,3(*t*-Bu)	0.018	0.021	0.018	0.021	0.017	0.018	0.018	0.019	0.017
2	0.105	0.121	0.094	0.120	0.086	0.088	0.088	0.088	0.090
4,6	0.616	0.646	0.645	0.654	0.664	0.666	0.661	0.662	0.662
5(*t*-Bu)[c])	0.003	0.003	0.003	0.003	–	–	–	–	–

[a]) The meaning of $H\mu$ is H–C(x), H–C(y), whereas only x and y are given in the *Table*.

[b]) Experimental error: ±0.001, ±0.002 and ±0.005 mT for $a_{H1,3(t\text{-}Bu)}$, a_{H2} and $a_{H4,6}$, respectively.

[c]) Splitting unresolved; with the solvent MTHF, the value $a_{H5,(t\text{-}Bu)} = 0.003 \pm 0.001$ mT could be estimated from the line-widths in the ESR. spectra.

Experimental Part. - The synthesis of 1,3,5-tri-*t*-butylpentalene (II) has been described elsewhere [3].

The radical anion $II^{\ominus}$ was produced by reaction of II with an alkali metal (sodium or potassium) in 2-methyltetrahydrofuran (MTHF) and in a 5:1 mixture of 1,2-dimethoxyethane (DME) with hexamethylphosphoric triamide (HMPA). In addition, $II^{\ominus}$ was generated electrolytically in dimethylformamide (DMF), dimethylsulfoxide (DMSO) and methylene chloride which contained tetraalkylammonium ($Et_4N^{\oplus}$ or $Bu_4N^{\oplus}$) perchlorate as the supporting salt.

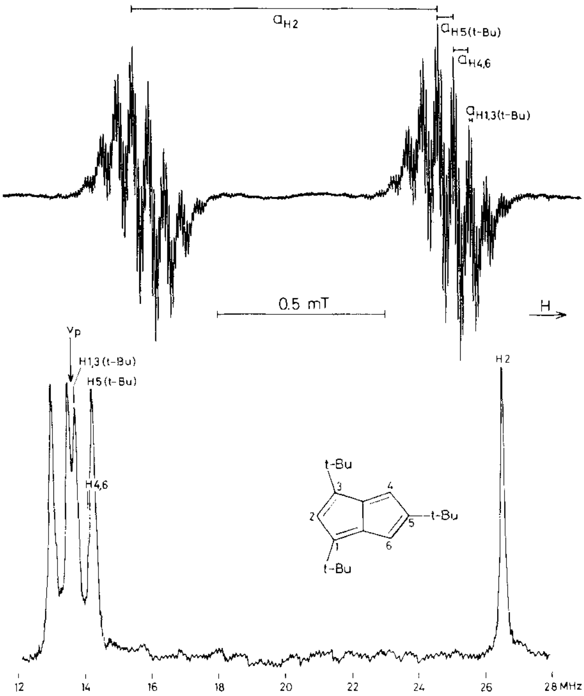


Fig. 2. *ESR. and ENDOR. spectra of the radical cation of 1,3,5-tri-*t*-butylpentalene (II).* Solvent: CH_2Cl_2; temp.: 283 (ESR.) and 243 K (ENDOR.). ν_P = frequency of the free proton.

Table 2. *Proton coupling constants,* $a_{H\mu}$[a]) in mT, *for the radical cation of 1,3,5-tri-*t*-butylpentalene (II)*[b])

Solvent Counterion	CH_2Cl_2 [c])	CH_3NO_2 [c])	CH_2Cl_2 $ClO_4^{\ominus}$	$CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ $CF_3COO^{\ominus}$
Temp. (K)	283	283	213	293
μ = 1,3(*t*-Bu)	0.006	[d])	[d])	0.007
2	0.918	0.919	0.920	0.920
4,6	0.040	0.044[e])	0.046[e])	0.039
5(*t*-Bu)	0.045	0.044	0.046	0.044

[a]) The meaning of Hμ is H—C(x), H—C(y), whereas only x and y are given in the *Table.*

[b]) Experimental error: ±0.001 mT for $a_{H\,1,3(t\text{-Bu})}$, $a_{H\,4,6}$ and $a_{H\,5(t\text{-Bu})}$, and ±0.005 mT for a_{H2}.

[c]) Radical cation produced by reaction with $AlCl_3$; counterion undetermined.

[d]) Splitting unresolved.

[e]) Difference between $a_{H\,4,6}$ and $a_{H\,5(t\text{-Bu})}$ not secured by analysis of the spectra.

The radical cation II$^{\oplus}$ was prepared by dissolving II in a 10:1:1 mixture of methylene chloride or nitromethane with trifluoroacetic acid and its anhydride, as well as by reaction with aluminium trichloride in methylene chloride or nitromethane. Electrolytic oxidation in methylene chloride with tetrabutylammonium perchlorate as the supporting salt also yielded II$^{\oplus}$, in confirmation of the report by *Johnson* [4].

Both radical ions, II$^{\ominus}$ and II$^{\oplus}$, formed very readily under all aforementioned conditions and had half-lives of the order of hours below 293 K. Their *g*-factors were 2.0027 (II$^{\ominus}$ in DME/HMPA at 213 K) and 2.0026±0.0001 (II$^{\oplus}$ in CH_2Cl_2 at 273 K).

The cylindric cells employed in the electrolysis of II were those quoted in the previous papers dealing with the electrolytic reduction [5] and oxidation [6].

The ENDOR. spectra could be observed for the 'chemically', *i.e.*, non-electrolytically, produced radical ions in the temperature range from 163 to 273 K.

The spectrometer was a *Varian*-1700-ENDOR. system linked to a *Varian*-E9 ESR. instrument.

Results. - *Figure 1* shows the ESR. and ENDOR. spectra of the radical anion $\mathrm{II}^{\overset{\ominus}{\cdot}}$ in MTHF with $\mathrm{Na}^{\oplus}$ as the counterion. In this solvent, the proton coupling constants, a_{H_μ}, markedly depended on the nature of alkali metal cation and on the temperature. On the contrary, with the use of more polar solvents, such as DME/HMPA, DMF and DMSO, and/or tetraalkylammonium counterions, the corresponding values a_{H_μ} did not exhibit such a dependence. This finding is evident from *Table 1* which summarizes the proton hyperfine data observed for $\mathrm{II}^{\overset{\ominus}{\cdot}}$ under various conditions.

The ESR. and ENDOR. spectra of the radical cation $\mathrm{II}^{\overset{\oplus}{\cdot}}$, produced with $AlCl_3$ in CH_2Cl_2 are displayed in *Figure 2*. Within the limits of experimental error, the proton coupling constants a_{H_μ}, determined from these spectra, did not differ from those obtained upon generation of $\mathrm{II}^{\overset{\oplus}{\cdot}}$ by other methods. The pertinent data are collected in *Table 2*.

Comparison of the coupling constants a_{H_μ} derived in this work with the values reported by *Johnson* [4] reveals deviations which are beyond the range of experimental error; *e.g.*, the coupling constant $a_{H2} = 0.920 \pm 0.005$ mT found for $\mathrm{II}^{\overset{\oplus}{\cdot}}$ in CH_2Cl_2 at low temperatures *(Table 2)* is significantly different from the corresponding value of 0.88 mT quoted by that author. It is reasonable to assume that the present data are more precise than the previous ones.

In some experiments, during the electrolytic reduction of II in DMF or DMSO, occurrence of secondary and tertiary radical anions was observed, probably due to traces of air and/or protic impurities. The two species gave rise to well-defined ESR. spectra. That of the secondary radical anion was readily analyzed in terms of the coupling constants, 0.952 ± 0.004 and 0.436 ± 0.003 mT, each for two equivalent protons, and 0.017 ± 0.001 mT for 18 equivalent protons. The tertiary radical anion displayed a hyperfine pattern, consistent with the coupling constants, 0.928 ± 0.004 mT for two equivalent protons, 0.374 ± 0.003 mT for a single proton, and 0.013 ± 0.001 mT for 18 equivalent protons. The structures of the two subsequently formed species have not yet been clarified. Merely, the conspicuous small hyperfine splittings from 18 protons indicate the presence of two equivalent *t*-butyl substituents.

Discussion. - *General remarks.* The simplest MO model of pentalene (I) is an eight-membered π-perimeter which is perturbed by the introduction of a cross-link between two opposite centres. The first order perturbation removes the degeneracy of the two non-bonding perimeter orbitals in such way that the one classified as symmetric (Ψ_S) with respect to the mirror plane m passing through these centers becomes bonding, whereas its antisymmetric counterpart (Ψ_A) retains the non-bonding character *(Fig. 3)*. Since Ψ_S and Ψ_A turn into the HOMO and LUMO, respectively, of I, this compound is expected to have a moderately sized ionization potential [7], along with a very high electron affinity [8]. The ease of formation observed for both radical ions of the alkyl derivative II (see exper. part) is thus readily understood when, additionally, one accounts for the substituent effect of the three *t*-butyl groups. This effect considerably lowers the ionization potential (7.11 eV, from the PE. spectrum of II [7]) without excessively impairing the electron affinity (half-wave $E_{1/2}$ of -1.46 V *vs.* SCE from the polarographic reduction of II [4]).

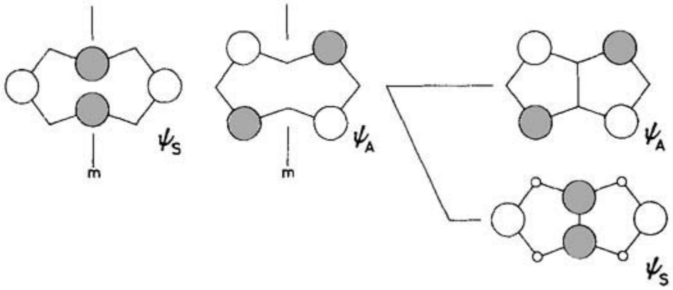


Fig. 3. *Non-bonding orbitals of the eight-membered π-perimeter and removal of their degeneracy by the introduction of a bond linking two opposite centres.* The areas of the circles are proportional to the squares of the LCAO-coefficients. Blank and shaded areas symbolize different signs of these coefficients.

Table 3. *π-Spin populations* ρ_μ[a]) *and proton coupling constants,* $a_{H\mu}$[b]) in mT[c]), *calculated for the radical ions of pentalene (I) and its 1,3,5-tri-*t*-butyl derivative (II)*

	$\mathrm{I}^{\ominus\cdot}$		$\mathrm{I}^{\oplus\cdot}$		$\mathrm{II}^{\ominus\cdot}$		$\mathrm{II}^{\oplus\cdot}$	
	ρ_μ	$a_{H\mu}$	ρ_μ	$a_{H\mu}$	ρ_μ	$a_{H\mu}$	ρ_μ	$a_{H\mu}$
μ = 1,3	+0.307	−0.737	−0.038	+0.105	+0.343	(0.017)[d])	−0.038	(0.005)[d])
2	−0.072	+0.174	+0.339	−0.947	−0.076	+0.182	+0.334	−0.935
4,6	+0.307	−0.737	−0.038	+0.105	+0.262	−0.629	−0.022	+0.061
5	−0.072	+0.174	+0.339	−0.947	−0.068	(0.003)[d])	+0.338	(0.047)[d])
3a,6a	−0.041	-	+0.237	-	−0.033	-	+0.224	-

[a]) Calculated according to the procedure of *McLachlan* (λ = 1.0).

[b]) The meaning of $H\mu$ is H−C(x), H−C(y), whereas only x and y are given in the *Table*.

[c]) Obtained from the calculated values ρ_μ with the use of the *McConnell* equation where Q = −2.4 (radical anions) and −2.8 mT (radical cations).

[d]) Obtained from the calculated values ρ_μ with the use of relationship (2) where $|Q_{t\text{-Bu}}| = 0.05$ ($\mathrm{II}^{\ominus\cdot}$) and 0.14 mT ($\mathrm{II}^{\oplus\cdot}$).

π-Spin distribution. Table 3 contains the π-spin populations ρ_μ calculated for the radical ions of pentalene (I) and its 1,3,5-tri-*t*-butyl derivative (II) by the *McLachlan* procedure (λ = 1.0) [9], whereby, in the case of $\mathrm{II}^{\ominus\cdot}$ and $\mathrm{II}^{\oplus\cdot}$, a value of α-0.3β was adopted for the HMO parameter α_μ of the *t*-butyl substituted centres μ = 1,3 and 5. Also listed are the predicted coupling constants, $a_{H\mu}$, of the ring protons in the four radical ions. They resulted from the π-spin populations ρ_μ with the use of the *McConnell* equation [10]

$$a_{H\mu} = Q\,\rho_\mu \qquad (1)$$

where Q = −2.4 and −2.8 mT for the radical anions and cations, respectively. As is evident from the comparison of these values $|a_{H\mu}|$ obtained for $\mathrm{II}^{\ominus\cdot}$ and $\mathrm{II}^{\oplus\cdot}$ with their observed counterparts *(Tables 1* and *2)*, a fair agreement is achieved between the theory and experiment. This agreement gives some credit to the simple MO model which predicts that the π-spin distributions should not be greatly altered on passing from $\mathrm{I}^{\ominus\cdot}$ and $\mathrm{I}^{\oplus\cdot}$ to $\mathrm{II}^{\ominus\cdot}$ and $\mathrm{II}^{\oplus\cdot}$, respectively. According to such prediction, the hyperfine data, a_{H2} and $a_{H4,6}$, found for the radical anion and cation of the 1,3,5-tri-*t*-butylpentalene (II), are representative for the experimentally unavailable coupling constants of the corresponding protons in the radical ions of the parent compound (I) itself.

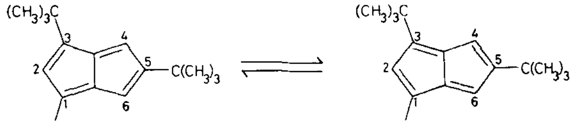
It is noteworthy that the coupling constants $a_{H_{\mu(t\text{-Bu})}}$ of the *t*-butyl protons in $\mathrm{II}^{\ominus\cdot}$ and $\mathrm{II}^{\oplus\cdot}$ appear to be roughly proportional to the π-spin populations ρ_{μ} at the substituted centres μ. The proportionality factors $|Q_{t\text{-Bu}}|$ in such a relationship

$$a_{H\mu(t\text{-Bu})} \approx Q_{t\text{-Bu}}\,\rho_{\mu} \qquad (2)$$

amount to *ca.* 0.05 mT for the radical anion and *ca.* 0.14 mT for the radical cation. These values are somewhat lower and higher, respectively, than those proposed for *t*-butyl protons in derivatives of the neutral anilino and phenoxy radicals (0.08 to 0.11 mT) [11]. A general use of eq. (2) has, however, been discouraged by some authors [12].

Dependence of the coupling constants on experimental conditions. The coupling constants $a_{H_{\mu}}$ for the radical anions of non-alternant hydrocarbons have been found to be much more sensitive to variations in solvent, counterion and temperature than the corresponding values for alternant species [13]. The best known examples are the radical anions of azulene [13] [14] and acenaphthylene [13] [15] to which, according to the present studies, $\mathrm{II}^{\ominus\cdot}$ can also be added. For $\mathrm{II}^{\ominus\cdot}$, as well as for those two radical anions, the phenomenon responsible for this sensitivity must be the association with the counterion. Such a statement is supported by the data in *Table 1* which demonstrate that the coupling constants become almost independent of experimental conditions when polar solvents and/or bulky tetraalkylammonium cations are involved, *i.e.*, when ion pairing is loose. The same arguments can be advanced in the case of $\mathrm{II}^{\oplus\cdot}$ to account for the relative insensitivity of the coupling constants $a_{H_{\mu}}$ to changes in environment and temperature *(Table 2)*, since $\mathrm{II}^{\oplus\cdot}$, as the radical cations in general, is produced under conditions where its association with the counterion is weak.

Bond alternation. Quantum chemical models predict that the 4n π-electron perimeter of pentalene (I) should exhibit alternating essential double and single bonds ([7] and ref. therein). This prediction has been borne out by experiment for the 1,3,5-tri-*t*-butyl derivative (II) in solid state with the use of the X-ray crystallography [16]. Furthermore, an interconversion between the two *Kekulé* structures II and II′ has recently been found by *Oth & Müllen* to take place in solution (*cf.* footnote 20 in [7]).



II II′

The activation energy for the bond shift occurring in such an interconversion amounts to *ca.* 16 kJ/mol, as estimated from the ^{13}C-NMR. spectra of II at 93 K. An analogous study should be practicable at considerably higher temperature in the ESR. and ENDOR. spectra of the radical ions $\mathrm{II}^{\ominus\cdot}$ and $\mathrm{II}^{\oplus\cdot}$, since the hyperfine time-scale (10^6 to 10^8 s^{-1}) is, in the case of such low barriers, more favourable than that of the ^{13}C chemical shift (10^2 to 10^3 s^{-1}). The radical anion $\mathrm{II}^{\ominus\cdot}$ seems to be particularly well suited for the studies of the phenomenon in question, because of the large magnitude of the coupling constants $a_{H4,6}$ ($= a_{H-C(4),H-C(6)}$) observed for the two protons which are non-equivalent in II and II′. However, the ESR. and ENDOR. spectra of $\mathrm{II}^{\ominus\cdot}$ in MTHF taken above 163 K failed to reveal specific line-broadening which could be attributed to this non-equivalency. Neither was such an effect observed by extending the temperature range for the ESR. studies down to 133 K through the use of diethyl ether as the solvent.

Presumably, bond alternation is less pronounced in the radical anion $II^{\dot{\ominus}}$ than in the neutral compound II and/or the activation energy for the bond shift is lower in the former case than in the latter. This statement should also hold for the radical cation $II^{\dot{\oplus}}$ with respect to II, since it is in line with the intermediate positions of the radical ions between the neutral compounds and diions. Although $II^{2\ominus}$ and $II^{2\oplus}$ have not yet been prepared [4], NMR. studies of the pentalene dianion ($I^{2\ominus}$) [8], the cyclooctatetraene dianion [17] and several methyl substituted cyclooctatetraene dications [18] indicate the absence of bond alternation in the $(4n+2)$ π-electron perimeters of these species.

This work was supported by the *Swiss National Science Foundation* (project 2.711.77). Financial assistance by *Ciba-Geigy SA*, *Sandoz SA* and *F. Hoffmann-La Roche & Cie. SA*, Basel is also acknowledged.

REFERENCES

[1] See *e.g.*, *K. Hafner*, in 'The Chemistry of Nonbenzenoid Aromatic Compounds', Pure appl. Chemistry *28*, 153 (1971); *T. Nakajima*, ibid., 219; see also: *R. Zahradnik*, in 'Nonbenzenoid Aromatics' (J.P. Snyder, ed.), Vol.II, pp. 1–80, Academic Press, New York 1971.

[2] *R. Bloch, R.A. Marty & P. de Mayo*, J. Amer. chem. Soc. *93*, 3071 (1971); Bull. Soc. chim. France *1972*, 2031; *K. Hafner, R. Dönges, E. Goedecke & R. Kaiser*, Angew. Chem. *85*, 362 (1973); Angew. Chem. Int. Ed. Engl. *12*, 337 (1973).

[3] *K. Hafner & H.U. Süss*, Angew. Chem. *85*, 626 (1973); Angew. Chem. Int. Ed. Engl. *12*, 575 (1973).

[4] *R.W. Johnson*, J. Amer. chem. Soc. *99*, 1461 (1977).

[5] *F. Gerson, H. Ohya-Nishiguchi & Ch. Wydler*, Angew. Chem. *88*, 617 (1976); Angew. Chem. Int. Ed. Engl. *15*, 552 (1976).

[6] *J. Bruhin, F. Gerson & H. Ohya-Nishiguchi*, Helv. *60*, 2471 (1977).

[7] *P. Bischof, R. Gleiter, K. Hafner, K.H. Knauer, J. Spanget-Larsen & H.U. Süss*, Chem. Ber. *111*, 932 (1978).

[8] *T.J. Katz, M. Rosenberger & R.K. O'Hara*, J. Amer. chem. Soc. *86*, 249 (1964).

[9] *A.D. McLachlan*, Mol. Physics *3*, 233 (1960).

[10] *H.M. McConnell*, J. chem. Physics *24*, 632 (1956).

[11] *N.M. Atherton, E.J. Land & G. Porter*, Trans. Faraday Soc. *59*, 818 (1963).

[12] *C. Trapp, C.A. Tyson & G. Giacometti*, J. Amer. chem. Soc. *90*, 1394 (1968).

[13] See, e.g., *F. Gerson & J.H. Hammons*, in 'Nonbenzenoid Aromatics' (J.P. Snyder, ed.), Vol.II, pp.82–166, Academic Press, New York 1971.

[14] *I. Bernal, P.H. Rieger & G.K. Fraenkel*, J. chem. Physics *37*, 1489 (1962); *A.H. Reddoch*, ibid. *41*, 444 (1964); *43*, 225 (1965).

[15] *M. Iwaizumi & T. Isobe*, Bull. chem. Soc. Japan *37*, 1651 (1964); *F. Gerson & J. Heinzer*, unpublished data.

[16] *B. Kitschke & H.J. Lindner*, Tetrahedron Letters *1977*, 2511.

[17] *T.J. Katz*, J. Amer. chem. Soc. *82*, 3784 (1960); *S.Z. Goldberg, K.N. Raymond, C.A. Harmon & D.H. Templeton* ibid. *96*, 1348 (1974).

[18] *G.A. Olah, J.S. Staral, G. Liang, L.A. Paquette, W.P. Melega & M.J. Carmody*, J. Amer. chem. Soc. *99*, 3349 (1977).