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## 104. The Structure of 2,5-Semiquinones derived from 1,6-Bridged [10] Annulenes

by **F. Gerson<sup>1)</sup>**, **K. Müllen<sup>1)</sup>** and **E. Vogel<sup>2)</sup>**

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, and Organisch-Chemisches Institut der Universität Köln, Zülpicher Strasse 47, 5 Köln, Germany

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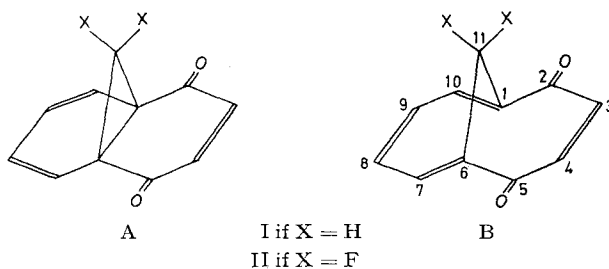
*Summary.* ESR. spectra are reported for the radical anions of the diketones I and II (see below), recently prepared from 1,6-methano[10]annulene and its 11,11-difluoro-derivative, respectively [1]. The  $\pi$ -spin populations of I<sup>⊖</sup> and II<sup>⊖</sup> are shown to be incompatible with the structure A an enedione-norcaradiene. Although the alternative structure B of a [10]annulene-quinone is acceptable for both I<sup>⊖</sup> and II<sup>⊖</sup>, the ESR. data is more satisfactorily rationalized in terms of a structure 'intermediate' to A and B. This is particularly true for the radical anion I<sup>⊖</sup>, for which the  $\pi$ -spin populations suggest a structural 'shift' B → A relative to II<sup>⊖</sup>. Structures A and B were postulated [1] for the neutral diketones I and II, respectively.

The diketones I and II obtained [1] from 1,6-methano[10]annulene and its 11,11-difluoro-derivative, respectively, are potentially 2,5-quinones with structure B; the alternative A is essentially an enedione-norcaradiene.

The electronic spectrum of II is shifted slightly to lower energies relative to that of I, indicating more extensive  $\pi$ -electron delocalization in the former compound. The proton magnetic resonance spectra of the two diketones are even more informative. Whereas the spectrum of II is consistent with the quinone structure B, that of I strongly favours the alternative A [1].

<sup>1)</sup> Universität Basel.

<sup>2)</sup> Universität Köln.



Reporting on the ESR. data of the radical anion  $I^{\ominus}$ , the authors [2] proposed structure B for  $I^{\ominus}$ , in contrast to that of the neutral diketone I. In the present paper we describe the ESR. spectra of both radical anions  $I^{\ominus}$  and  $II^{\ominus}$  and discuss their structures in terms of a simple MO.-model.

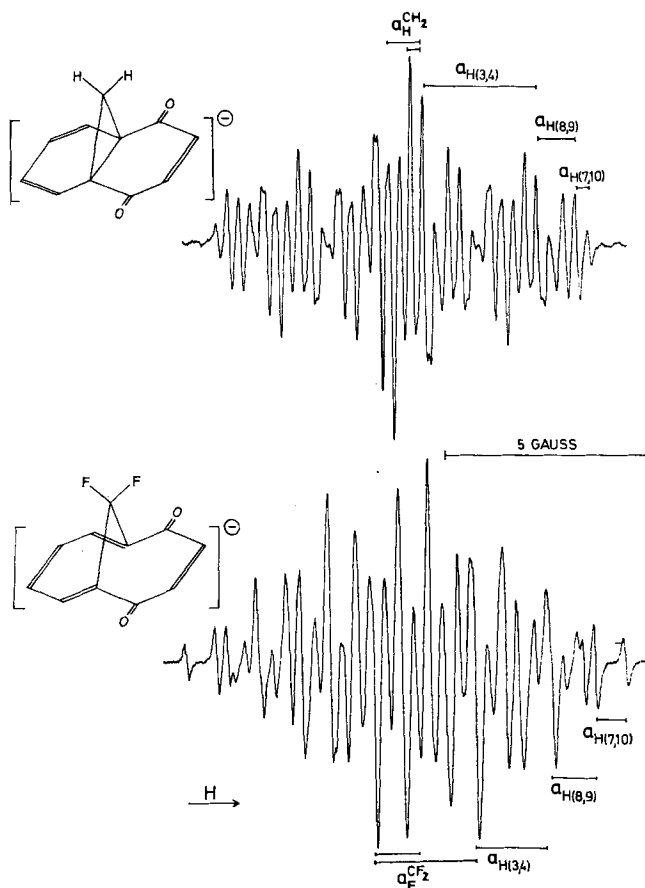


Fig. 1. ESR. spectra of the radical anions  $I^{\ominus}$  and  $II^{\ominus}$ . Solvent, dimethylformamide; gegenion,  $(C_2H_5)_4N^{\oplus}$ ; temp.  $-60^{\circ}$

Formulae represent the structures of the neutral diketones as established by proton magnetic resonance [1]

**Results.** – *ESR. spectra.* The radical anions  $I^\ominus$  and  $II^\ominus$  were generated electrolytically in a 0.1M solution of tetraethylammonium perchlorate in N,N-dimethylformamide (DMF). The stabilities of  $I^\ominus$  and  $II^\ominus$  are markedly different: whereas the former decays rapidly at room temperature, the latter can be conveniently investigated even at  $+60^\circ$ . The two radical anions also differ in the temperature-sensitivity of their ESR. spectra: whereas the splitting pattern of  $I^\ominus$  does not appreciably alter within the range of  $-60^\circ$  to  $+25^\circ$ , striking changes are observed in the spectrum of  $II^\ominus$  if the temperature is raised above  $-20^\circ$ . These changes will be discussed in a separate paper [3]. Fig. 1 shows the spectra recorded at  $-60^\circ$ . The coupling constants of the magnetic nuclei are listed in tab. 1; their experimental error is about  $\pm 0.01$  G. The values in brackets are those measured previously under different conditions [2].

Table 1. *Coupling constants (in G) of protons and  $^{19}\text{F}$  nuclei in the radical anions  $I^\ominus$  and  $II^\ominus$*

$I^\ominus$			$II^\ominus$		
coupling constant	nr of nuclei		coupling constant	nr of nuclei	position
$a_{\text{H}(\mu)}$ { 2.73 (2.85) 0.89 (0.78) 0.28 (0.25)	2H 2H 2H		$a_{\text{H}(\mu)}$ { 1.78 1.03 0.76	2H 2H 2H	3,4 8,9 7,10
$a_{\text{H}}^{\text{CH}_2}$ { 0.82 (0.78) 0.28 (0.25)	1H 1H		$a_{\text{F}}^{\text{CF}_2}$ { 2.43 1.08	1F 1F	11 11

*Coupling constants.* The assignment of the coupling constants  $a_{\text{H}(\mu)}$  of the three pairs of equivalent protons attached to  $\pi$ -centres  $\mu$ , is based on MO.-models (discussed below). The relevant  $\pi$ -spin populations  $\rho_\mu$ , calculated by use of these models, follow the sequence:  $\rho_3 = \rho_4 > \rho_8 = \rho_9 > \rho_7 = \rho_{10}$ . An analogous sequence  $a_{\text{H}(3)} = a_{\text{H}(4)} > a_{\text{H}(8)} = a_{\text{H}(9)} > a_{\text{H}(7)} = a_{\text{H}(10)}$  is required for the coupling constants  $a_{\text{H}(\mu)}$  in order to achieve an optimum correlation between the experimental and calculated values. This leads to the assignment suggested in Table 1 and used throughout this paper.

For the coupling constants  $a_{\text{H}}^{\text{CH}_2}$  and  $a_{\text{F}}^{\text{CF}_2}$  of the two non-equivalent nuclei in the bridging groups (position 11), a *syn*- or *anti*-configuration (with regard to the enedione  $\pi$ -system) has not been postulated. It should be noted that the lowest antibonding  $\pi$ -orbital of the enedione, which contains the bulk of the unpaired electron density (see below), has a nodal plane passing through the two nuclei. This situation contrasts with that of the corresponding protons in the bridged 1,2-diones [4].

**Discussion.** – *Preliminary comments.* In Table 2 which shows the structural formulae of enediones I to V, the number indicated under each formula is the  $\pi$ -spin population  $\rho_3$  ( $= \rho_4$ ) at the carbon centre 3 in each radical anions  $I^\ominus$  to  $V^\ominus$ . The  $\rho_3$  values for  $I^\ominus$  and  $II^\ominus$  have been calculated from the *McConnell* equation (1) [5] using the

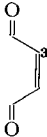
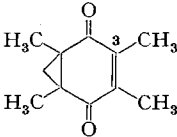
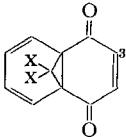
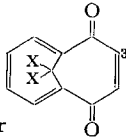
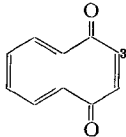
$$a_{\text{H}(\mu)} = Q \cdot \rho_\mu \quad (1)$$

coupling constants  $a_{\text{H}(3)}$  ( $= a_{\text{H}(4)}$ ) listed in Table 1. An analogous relation ship (2) [6] between

$$a_{\text{H}}^{\text{CH}_2} = \frac{1}{2} B \cdot \rho_\mu \quad (2)$$

the coupling constant  $a_{\text{H}}^{\text{CH}_3}$  of protons in a methyl substituent and the  $\pi$ -spin population  $\rho_{\mu}$  at the substituted center  $\mu$  gives the  $\rho_3$  value for  $\text{IV}^{\ominus}$  ( $a_{\text{H}}^{\text{CH}_3} = 5.20 \text{ G}$  [2]). The factors  $|Q|$  and  $\frac{1}{2}|B|$  have been given a common absolute value of  $22.5 \text{ G}^3$ , and all resulting  $\pi$ -spin populations  $\rho_3$  are assumed to be positive. For the unknown radical anions  $\text{III}^{\ominus}$  and  $\text{IV}^{\ominus}$  the  $\rho_3$  values have been computed by the *McLachlan* procedure [9] using the heteroatom parameters  $\alpha_0 = \alpha + 1.2\beta$  and  $\beta_{\text{CO}} = 1.56\beta$  advanced by *Vincow & Fraenkel* [10] for *p*-semiquinones. The *McLachlan* number  $\lambda$  has its usual value, 1.2.

 Table 2.  $\pi$ -spin populations  $\rho_3$  in the radical anions  $\text{I}^{\ominus}$  to  $\text{V}^{\ominus}$ 

				
III	IV	I (X = H)	II (X = F)	V
$\rho_3$ 0.248	0.231	0.121	0.079	0.071

MO.-models give evidence that the  $\pi$ -spin populations  $\rho_3$  are very sensitive to the conjugation between the enedione moiety and the rest of the molecule; therefore it may be assumed that the  $\rho_3$  value is a rough indicator of the extent of such a conjugation. Comparison of the spin populations  $\rho_3$  in the radical anions  $\text{IV}^{\ominus}$ ,  $\text{I}^{\ominus}$  and  $\text{II}^{\ominus}$  with the corresponding values for the borderline cases  $\text{III}^{\ominus}$  and  $\text{V}^{\ominus}$  leads to the following conclusions: (1) The unpaired electron in  $\text{IV}^{\ominus}$  is to a large extent localized in the enedione moiety. (2) In  $\text{I}^{\ominus}$  and  $\text{II}^{\ominus}$  it is considerably delocalized over the rest of the molecule; such delocalization, however, seems to be more extensive in  $\text{II}^{\ominus}$  than in  $\text{I}^{\ominus}$ .

The alternative structures A and B for the radical anions  $\text{I}^{\ominus}$  and  $\text{II}^{\ominus}$  will now be discussed in more detail, making use for the coupling constants  $a_{\text{H}(\mu)}$  of the protons attached to centres  $\mu$ . The constants ( $a_{\text{H}}^{\text{CH}_3}$  or  $a_{\text{F}}^{\text{CF}_3}$ ) of the nuclei in the bridging groups will be left out of discussion, since in this case there is no known clear-cut relationship between the values of  $a_{\text{H}}^{\text{CH}_3}$  or  $a_{\text{F}}^{\text{CF}_3}$  and the  $\pi$ -spin populations  $\rho_{\mu}$ .

*Structure A.* Fig. 2 shows the HMO.-energy levels of the enedione III ( $\alpha_0 = \alpha + 1.2\beta$ ;  $\beta_{\text{CO}} = 1.56\beta$ ) and 1,3-butadiene. The antibonding *Walsh* levels of cyclopropane [11] are also depicted. They have been either determined by photoelectron spectroscopy [12] (bonding levels) or computed by the Extended *Hückel* method [13] (antibonding level); the energies are approximately adapted to the HMO.-scale. All levels in fig. 2 are classified as symmetric (S) or antisymmetric (A) with regard to the mirror plane *m* common to the diketones I to V. The additional unpaired electron in a system containing the enedione III, cyclopropane and 1,3-butadiene moieties occupies primarily the lowest antibonding level A of III.

Figure 2 shows that a mixing of *Walsh* and/or butadiene  $\pi$ -orbitals with the singly occupied orbital of III should be very small, since there are no cyclopropane

<sup>3)</sup> This  $|Q|$  value of (22.5 G) is the total spread of the ESR. spectrum of the benzene radical anion [7]. A nearly identical absolute value  $\frac{1}{2}|B| = 22.4 \text{ G}$  has been derived from the spectra of the radical anions of dimethylnaphthalenes [8].

and butadiene levels A of similar energy. Indeed, a perturbation treatment indicates that only a few percent of the total unpaired electron density is transferred from the lowest antibonding orbital of III to the cyclopropane and butadiene orbitals, even assuming a 'bisected' conformation adopted for the cyclopropane ring<sup>4)</sup> and/or a substantial interaction between the non-conjugated enedione and butadiene  $\pi$ -systems<sup>5)</sup>.

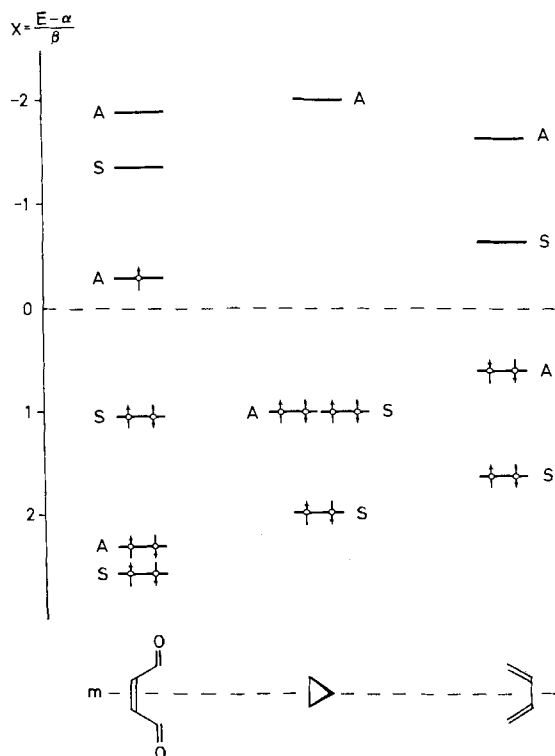


Fig. 2. Energy diagrams of the enedione III, cyclopropane and 1,3-butadiene

The arguments advanced here apply—irrespective of symmetry—to most radical anions containing a  $\pi$ -system linked to a cyclopropyl ring, since the energetic position of the *Walsh* orbitals impedes 'mixing' with the lowest antibonding  $\pi$ -orbitals. In contrast, mixing of the upper filled *Walsh* orbitals with the highest bonding  $\pi$ -orbitals is energetically favoured. Consequently, the cyclopropyl substituents in  $\pi$ -electron systems tend to assume the effective 'bisected' conformation<sup>4)</sup> in radical cations, but not in radical anions [16].

- <sup>4)</sup> In the 'bisected' conformation the plane of the cyclopropane ring is parallel to the  $2p_z$ -axes of the  $\pi$ -orbitals. In this conformation, the *Walsh* orbitals interact most effectively with the  $\pi$ -orbitals, whereas an analogous interaction in the 'perpendicular' conformation is negligible. The maximal interaction energy has been estimated for bullvalene as 1.9 eV ( $\approx 0.8\beta$ ) [14].
- <sup>5)</sup> The interaction energy between non-conjugated double bonds (homoconjugation) amounts to 1.0, 0.85 and 0.6 eV (0.25 to 0.4 $\beta$ ) for 1,4-cyclohexadiene, [2,2,2]octadiene and norbornadiene, respectively [15].

The suggestion (see comment (1), p. 1049) that the unpaired electron should be largely localized in the enedione moiety of  $IV^\ominus$  is thus supported by conclusions drawn from the energy scheme in fig. 2. The same conclusions oppose structure A for  $I^\ominus$ , since—according to comment (2) (p. 1049)—a substantial delocalization of the unpaired electron, from the enedione moiety to the rest of the molecule, should prevail in this radical anion. The structure A is even less acceptable for  $II^\ominus$  for which the unpaired electron should be more extensively delocalized than for  $I^\ominus$ . The incompatibility of structure A for  $II^\ominus$  with such a delocalization is supported by considerations of the energy scheme analogous to those applied to  $I^\ominus$ . (Because of the presence of the two fluorine atoms in  $II^\ominus$ , the *Walsh* energy levels in this case differ from those used for cyclopropane in fig. 2.)

*Structure B.* Idealized  $\pi$ -electron systems of the diketones I and II, having the structure B, are represented by the [10]annulene-quinone V (tab. 2): more realistic models are required (however) to account for structural differences between V and the actual  $\pi$ -systems in I and II. Since such differences arise from the bridging of the  $\pi$ -systems, they primarily affect the bridged centres and the adjacent bonds. The following effects have to be considered:

1. Deviation of the  $\pi$ -electron system from planarity. This effect is most pronounced in the bonds 1-2, 5-6, 6-7 and 10-1. As shown by molecular models, the

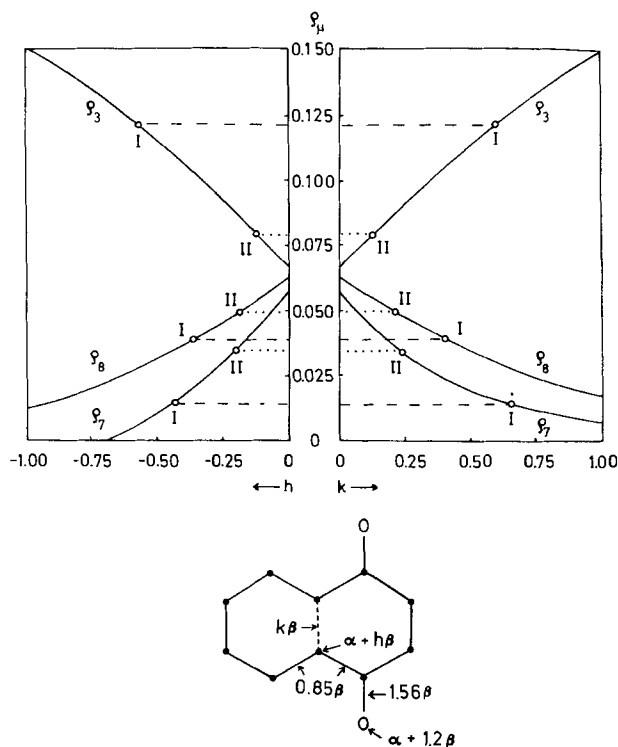


Fig. 3.  $\pi$ -spin populations in the radical anions  $I^\ominus$  and  $II^\ominus$  as functions of the HMO parameters  $\alpha_1 = \alpha_6 = \alpha + h\beta$  (left) and  $\beta_{1-6} = h\beta$  (right)

twisting angles of the two  $2p_z$ -axes flanking one bond are about  $30^\circ$ . A parameter  $\beta_{1-2} = \beta_{5-6} = \beta_{6-7} = \beta_{10-1} = \beta \cdot \cos 30^\circ (\approx 0.85\beta)$  has therefore been adopted in all calculations.

2. *Coulomb* repulsion between the  $\pi$ -electron charges at the bridged centres. In more refined MO.-methods like PPP., this effect operates through the parameter  $\gamma_{1-6}$  which depends on the distance between the centres 1 and 6. In our model, it has been simulated by a variable parameter  $\alpha_1 = \alpha_6 = \alpha + h\beta$  with  $-1 < h < 0$ .

3. Substituent effects of the bridging  $\text{CH}_2$  or  $\text{CF}_2$  groups. The character and direction of these effects are problematic. Whereas the  $\text{CH}_2$  group in  $\text{I}^\ominus$  can be considered as electron repelling [17], the effect of  $\text{CF}_2$  group in  $\text{II}^\ominus$  is questionable. By analogy with heteroatom bridged [10]annulenes and [74]annulenes, and guided by the results of CNDO.-calculations [18], one may assume that the overall effect of this group on the  $\pi$ -system is also electron-repelling. Although the substituent effect has not been explicitly taken into account, its inductive component is implicitly allowed for in the parameter  $\alpha_1 = \alpha_6 = \alpha + h\beta$  mentioned above.

4. Weak  $\pi$ -bonding between the bridged centres. This depends on both the 1-6 distance and the twisting angle of the relevant  $2p_z$ -axes, and is introduced into the model by a variable parameter  $\beta_{1-6} = k\beta$  with  $0 < k < 1$ .

Fig. 3 shows the *McLachlan*  $\pi$ -spin populations  $\varrho_\mu$  at the proton bearing centres  $\mu$  of  $\text{I}^\ominus$  and  $\text{II}^\ominus$  as a function of the parameters  $\alpha_1 = \alpha_6 = \alpha + h\beta$  or  $\beta_{1-6} = k\beta$ . As expected, a decrease in  $h$  or an increase in  $k$  reduces the extent of delocalization of the unpaired electron from the enedione moiety to the rest of the  $\pi$ -system. This reduction is indicated by the rise in the spin population  $\varrho_3 (= \varrho_4)$  at the expense of  $\varrho_8 (= \varrho_9)$  and  $\varrho_7 (= \varrho_{10})$ . Interestingly, the  $\varrho_\mu$  values computed either with  $0 > h > -1$  or with  $0 < k < 1$  are almost equal if  $|h| = k$ .

A comparison is also made in fig. 3 between the calculated  $\varrho_\mu$  values and the corresponding  $\pi$ -spin populations obtained from the coupling constants  $a_{\text{H}(\mu)}$  in tab. 1 by means of the *McConnell* equation ( $|Q| = 22.5 \text{ G}$ ). Again, all these 'experimental' spin populations have been assumed to be positive. They are symbolized in fig. 3 by dotted ( $\text{I}^\ominus$ ) and dashed ( $\text{II}^\ominus$ ) horizontal lines. It is evident that correlation between the 'experimental' and calculated  $\pi$ -spin populations is best when

$$h \approx -0.50 \text{ or } k \approx 0.50 \text{ for } \text{I}^\ominus,$$

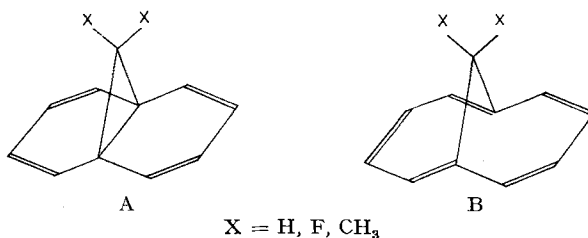
and

$$h \approx -0.15 \text{ or } k \approx 0.15 \text{ for } \text{II}^\ominus.$$

An interpretation of this result in terms of the effects 2 and 4 indicates a larger electronic interaction between the bridged centres in  $\text{I}^\ominus$  compared to  $\text{II}^\ominus$ : such an interaction consists of an enhanced *Coulomb* repulsion (2) and/or stronger bonding (4).

*Final remarks.* The last statement concerning the 1-6 interaction in  $\text{I}^\ominus$  and  $\text{II}^\ominus$  deserves further consideration, since it indicates that postulates about the  $\pi$ -spin populations in terms of 'pure' structures A and B might not be appropriate. The actual structures should be regarded rather as 'intermediate' between A and B, *i.e.* the energy minima for the two radical anions would not correspond exactly to the energies of either of the two 'pure' structures A or B. Presumably, analogous energy minima also occur in the case of the neutral diketones I and II, as well as in the

series of parent bridged [10]annulenes. In this series, the sensitivity of the structure to the nature of substituents X [19] in the bridging group  $CX_2$  indicates that the re-



levant potential energy wells between structures A and B must be rather shallow. It is evident that structural changes are facilitated by the similar 'shapes' of the atomic orbitals at the bridged centres in the structures A and B (fig. 4).

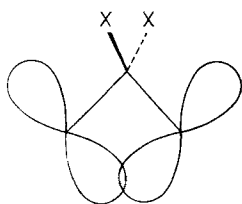


Fig. 4. Schematic representation of  $2p_z$ -AO's at the bridged centres 1 and 6 of [10]annulenes and their 2,5-diketones

A structural range between A and B should be continuous. Changes in the  $B \rightarrow A$  directions are expected to parallel a decrease in the interatomic distance and an increase in the interaction between the bridged centres 1 and 6. In the case of  $I^\ominus$  and  $II^\ominus$ , such changes are shown to result in a diminishing delocalization of the unpaired electron from the enedione moiety to the rest of the  $\pi$ -system. The  $\pi$ -spin populations  $\rho_\mu$  in the two radical anions can thus be rationalized more easily in terms of the postulated 'intermediate' structures than in terms of the pure 'structures' A and B. Whereas the latter procedure necessarily implies the same structure B for both radical anions ('pure' structure A being excluded on the grounds given above), differentiation between  $I^\ominus$  and  $II^\ominus$  becomes possible using the concept of 'intermediate' structures, according to which the radical anion  $II^\ominus$  exhibits a structure which is fairly close to B. The structure of  $I^\ominus$ , on the other hand, is shifted significantly towards A.

Direct comparison of the structures of  $I^\ominus$  and  $II^\ominus$  with those of the corresponding diketones I and II, is questionable, since the relevant information is based on different experimental data. As mentioned in the introduction, the structure A has been ascribed to I from its NMR. spectral data [1]. On the other hand, the ESR. data of  $I^\ominus$  suggest a structure 'intermediate' between A and B. This tendency towards the structure B, on formation of the radical anion, is expected on energetic grounds, since both delocalization of the additional electron and the antibonding contribution of the singly occupied orbital to the 1-6 bond order favour structure B rather than A.

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## 105. Recherches en vue de la synthèse de barbituriques organostannylés, II<sup>1)</sup>

par **Jean Claude Maire**<sup>2)</sup> et **Jurphaas Van Rietschoten**<sup>3)</sup>

Laboratoire des Organométalliques, Université de Provence, Centre de Saint-Jérôme  
13-Marseille (13<sup>e</sup>)

(18 III 71)

*Summary.* (a) The synthesis of 2,4,6-trioxo-1,3-di-tributylstannyl-hexahydropyrimidine is described.

(b) Trimethyltin hydride is found to add in a photochemical reaction to the terminal double bond of diethyl allyl malonate and allyl methyl malonate, giving respectively diethyl-(3-trimethylstannylpropyl)- (1) and diethyl-(3-trimethylstannylpropyl) (2) methyl-malonates.

Treated with urea under the usual conditions, (1) and (2) yield organostannyl barbituric acids.

Nous nous sommes proposé d'étudier la possibilité d'introduire des substituants organostanniques dans des molécules biologiquement actives. En vue d'effectuer des

<sup>1)</sup> I, voir [1]. L'ensemble de ce travail (parties I et II) a été réalisé dans le cadre d'un contrat de recherches avec la D.R.M.E. (n° 67 34 654 00 480 7501).

<sup>2)</sup> A qui doit être adressée toute correspondance.

<sup>3)</sup> Ce mémoire constitue une partie de la thèse de Docteur-Ingénieur de *J. Van Rietschoten* (Marseille, Juin 1970).