

# The Dimerization of 9-Cyanoanthracene Anion Radicals. A One- or Two-Step Reaction?

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Savéant, J.-M., 1988. The Dimerization of 9-Cyanoanthracene Anion Radicals. A One- or Two-Step Reaction? – Acta Chem. Scand., Ser. B 42: 721–727.

Dimerization of 9-cyanoanthracene anion radicals in the 10 position has been proposed to involve either a one-step bonding process or the prior formation of 'π complex', followed by σ-bond formation. Currently available thermodynamic and kinetic data in various solvents, including the enthalpic and entropic contributions to the free energy of the reaction and the free energies of activation do not provide direct evidence for either mechanism. However, modelling of the various attractive and repulsive forces in the dimer dianion, the transition state and the alleged 'π complex' indicates that the one-step mechanism is the most likely.

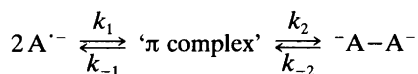
Why so much eagerness<sup>1-7</sup> in investigating the dimerization of electrogenerated 9-cyanoanthracene anion radicals? The reason is that this reaction is a particularly clean example of the dimerization of anion radicals in general: it yields a single product, the 10,10 dimer;<sup>6</sup> it is reversible,<sup>3,4</sup> thus allowing the investigation of the thermodynamics and kinetics of both the forward and backward processes; the enthalpic and entropic contributions to the characteristic free energies of reaction and of activation have been determined in various solvents.<sup>3,7</sup> Eagerness increased even more when a debate started about the one-step<sup>3,4</sup> versus two-step<sup>2,5,7</sup> character of this apparently simple reversible anion radical dimerization. The first alternative consists of a simple bonding process between two anion radicals,<sup>3,4</sup> whereas the second involves the formation of a 'π complex' prior to σ-bond formation.<sup>2,5,7</sup>

It should first be emphasized that the two mechanisms cannot be distinguished from each other through the investigation of the reaction kinetics by means, for example, of the standard electrochemical techniques (linear sweep voltammetry, double potential step chronoamperometry, direct or derivative cyclic voltammetry). A certain amount of time and effort have, however, been necessary to establish this essential preliminary point. Initially, deviations from the ki-

netic behavior expected for a simple electrodimmerization mechanism were found, serving as evidence against a one-step reaction and favoring a pre-association process.<sup>2</sup> As shown by further detailed studies,<sup>3,4,6</sup> this was the result of an artefact in the treatment of the electrochemical data arising from the neglect<sup>2</sup> of the interference of the backward reaction in the electrochemical kinetics. This conclusion now seems accepted, albeit tacitly.<sup>5,7</sup> We can thus start the discussion of the one-step versus two-step problem with the assertion that the dimerization of 9-cyanoanthracene anion radicals obeys the simple rate law:

$$\frac{1}{2} \frac{d[A^{\cdot-}]}{dt} = - \frac{d[-A-A^-]}{dt} \\ = -k_{\text{dim}}[A^{\cdot-}]^2 + k_{\text{diss}}[-A-A^-]$$

( $A^{\cdot-}$ ,  $-A-A^-$ : 9-cyanoanthracene anion radical and dimer dianion, respectively;  $k_{\text{dim}}$ ,  $k_{\text{diss}}$ : forward and backward rate constants). However, the two-step processes:



as well as the one-step process may conform to the above rate law. This is the case if it is as-

Table 1. Reaction and activation enthalpies<sup>a</sup> and entropies<sup>b</sup> in the dimerization of 9-cyanoanthracene anion radicals.

Solvent	$\Delta H_{\text{dim}}$	$\Delta S_{\text{dim}}$	$\Delta H_{\text{dim}}^{\ddagger}$	$\Delta S_{\text{dim}}^{\ddagger}$	$\Delta H_{\text{diss}}^{\ddagger}$	$\Delta S_{\text{diss}}^{\ddagger}$	Ref.
Pyridine	-13.3	-25	0.7	-32	14.0	-7	7
Butyronitrile	-13.1	-24	3.0	-24	16.1	0	7
<i>N,N</i> -Dimethylformamide	-14.5	-30	1.7	-29	16.2	1	7
Acetonitrile	-14.9	-28	2.2	-25	17.1	3	7
Propylene carbonate	-14.5	-28	-0.5	-37	14.0	-8	7
Hexamethylphosphoric triamide	-10.5	-20	4.5	-23	15.0	-3	7
Dimethyl sulfoxide	-12.8	-23	4.6	-18	17.4	5	3

<sup>a</sup>In kcal mol<sup>-1</sup>. <sup>b</sup>In eu (cal mol<sup>-1</sup> K<sup>-1</sup>).

sumed<sup>5,7</sup> that, since  $k_{-1}$  is much larger than  $k_2$ , the first reaction always remains at equilibrium. Then:

$$k_{\text{dim}} = K_1 k_2 \quad \text{and} \quad k_{\text{diss}} = k_{-2} \quad (K_1 = k_1/k_{-1}).$$

The assumption that the reaction consists of two successive steps rather than of a single step was based on the observation that the activation enthalpy of the forward reaction is very small, ranging from -0.5 to 4.5 kcal mol<sup>-1</sup> according to the solvent.<sup>3,5,7</sup> For such a two-step process the various characteristic free enthalpies, enthalpies and entropies can be expressed as:

$$\begin{aligned} \Delta G_{\text{dim}}^{\circ} &= \Delta G_1^{\circ} + \Delta G_2^{\circ}, & \Delta H_{\text{dim}} &= \Delta H_1 + \Delta H_2, \\ \Delta S_{\text{dim}} &= \Delta S_1 + \Delta S_2, & \Delta G_{\text{dim}}^{\ddagger} &= \Delta G_1^{\ddagger} + \Delta G_2^{\ddagger}, \\ \Delta H_{\text{dim}}^{\ddagger} &= \Delta H_1 + \Delta H_2^{\ddagger}, & \Delta S_{\text{dim}}^{\ddagger} &= \Delta S_1 + \Delta S_2^{\ddagger}, \\ \Delta G_{\text{diss}}^{\ddagger} &= \Delta G_{-2}^{\ddagger}, & \Delta H_{\text{diss}}^{\ddagger} &= \Delta H_{-2}^{\ddagger}, \\ \Delta S_{\text{diss}}^{\ddagger} &= \Delta S_{-2}^{\ddagger}. \end{aligned}$$

The small values of  $\Delta H_{\text{dim}}^{\ddagger}$  would thus result from the formation of the ' $\pi$  complex' being exothermic, the negative value of  $\Delta H_1$  compensating for the positive value of  $\Delta H^{\ddagger}$ .<sup>5,7</sup> Along these lines, the proof of the actual occurrence of the two-step reaction implies that the one-step dimerization cannot itself have such a small activation enthalpy. This is, in fact, not averted as discussed in the following, taking into account the values obtained for the other characteristic entropies and enthalpies of the reaction. Table 1 summarizes the available experimental data.

The dimerization of neutral radicals, being the reverse of the dissociation of a  $\sigma$ -bond, is ex-

pected to have a small activation energy, if any.<sup>8</sup> In the case of an anion radical, however, the coulombic repulsion may well cause a substantial activation enthalpy,  $\Delta H_{\text{dim}}^{\ddagger}$ , as well as a substantial increase of the reaction enthalpy,  $\Delta H_{\text{dim}}^{\ddagger}$ , over the value corresponding to the formation of the carbon-carbon  $\sigma$ -bond. As long as the two anion radicals are separated by solvent molecules, the repulsion between them is small. When they reach bonding distances and are thus located within the same solvent cage, an estimate of their repulsion energy,  $\Delta H_{\text{rep}}$ , can be obtained by considering that they are separated by vacuum. Thus:

$$\Delta H_{\text{dim}}^{\text{rep}} = \frac{332}{d} \text{ kcal mol}^{-1} \quad (1)$$

( $d$ : distance between the centers of negative charge in Å). As the two anion radicals come closer and closer together, coulombic repulsion tends to locate the negative charges as far apart as possible. An extreme situation, in this respect, would be for the negative charges to be located on the nitrogens of the cyano groups (Fig. 1). Then  $d = 11.6$  Å and thus  $\Delta H_{\text{dim}}^{\text{rep}} = 29$  kcal mol<sup>-1</sup>. This figure may in fact be underestimated since delocalization of the charge over each conjugated system 'resists' the location of the charge on the nitrile nitrogens. A very rough estimate of this effect will be described in the following, leading to an only slightly higher value.

At this stage, i.e., assuming that coulombic repulsion in the transition state and in the dimer dianion, and  $\sigma$ -bond formation in the dimer dianion are the only controlling factors, one might conclude that the one-step mechanism does not

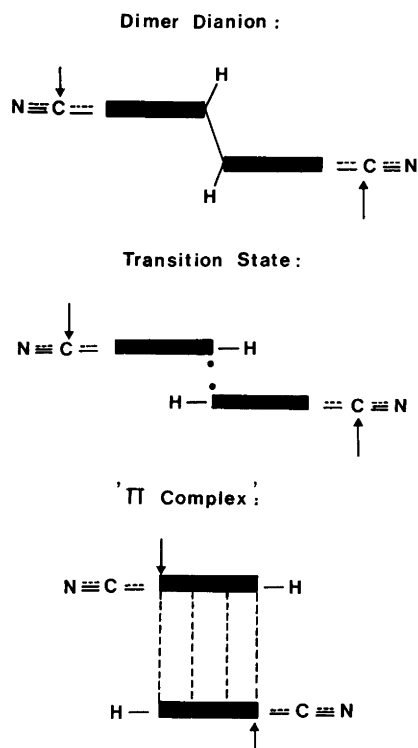


Fig. 1. Schematic side view of the dimer dianion, the transition state for the one-step reaction, and the 'π complex' for the two-step process. The vertical arrows indicate the location of the centers of negative charge.

occur since it involves an activation enthalpy much higher (ca. 30 kcal mol<sup>-1</sup>) than the experimental values.

However, another important influence is operative, namely the change in solvation on passing from the two anion radicals to the transition state and to the final dimer dianion, arising from the localization of the negative charge over a smaller and smaller portion of each monomeric moiety. Before detailing this point, let us note that a striking feature of the reaction and activation enthalpies and entropies is that the transition state resembles the initial state on enthalpy grounds and the final state on entropy grounds. This can be interpreted as follows. Coulombic repulsion, solvation of each anionic moiety, and translational and rotational partition functions are approximately the same in the transition state and in the final dimer dianion. As indicated in

Fig. 1, the essential difference between the dimer dianion and the transition state is the formation of the σ-bond. Furthermore, as shown in the following, coulombic repulsion and an increase in solvation upon passing from the two initial anion radicals to the transition state or to the final dimer dianion approximately compensate each other.

As regards reaction and activation entropies, at least a part of the total entropy loss (20 to 40 eu), on going from the initial state to the transition state or to the final state, results from the conversion of two molecules into one. A rough estimate of the ensuing entropy loss, regarding the anion radicals as spherical particles, leads (at 298 K) to:<sup>8</sup>

$$\Delta S_{\text{dim}}^{\text{tr}} = R \ln \left( 0.01 \frac{\sigma^2}{M^{1/2}} \right) = -8.6 \text{ eu}$$

(σ: distance between the two centers of mass, in Å, i.e., 4.45; M: molar mass of the monomer in g, i.e., 203). The term exp(ΔS<sub>dim</sub><sup>tr</sup>/R) is the equivalent of the 'steric factor' in terms of the collision theory of reaction rates. We note that |ΔS<sub>dim</sub><sup>tr</sup>| is significantly smaller than |ΔS<sub>dim</sub>| and |ΔS<sub>dim</sub><sup>#</sup>|. The steric factor, although markedly smaller than unity, cannot therefore entirely explain, as assumed before, why the dimerization is slow while having such a small activation enthalpy.<sup>4</sup> A significant fraction (10–20 eu) of the total entropy loss is thus caused by the increase of solvation resulting from the concentration of the negative charge that takes place upon going from the two initial anion radicals to the transition state or to the final dimer dianion. On this basis, let us now estimate the corresponding decrease in enthalpy, ΔH<sub>dim</sub><sup>solv</sup>, and the location of the center of charge in the transition state and dimer dianion, leading to a better value of ΔH<sub>dim</sub><sup>rep</sup> than that given above.

Table 2 contains the enthalpies, entropies and free enthalpies of solvation of four anions, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, in three non-aqueous solvents for which reliable data are available.<sup>9–12</sup> We note that the ratio of enthalpy to entropy of solvation is approximately constant for each solvent. The same is true for the product of the ionic radius and the solvation free enthalpy. From the first of these observations we can derive an estimate of ΔH<sub>dim</sub><sup>solv</sup>, ΔS<sub>dim</sub><sup>solv</sup>, the portion of the dimerization entropy corresponding to the increase of solvation, is obtained from:

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$$\Delta S_{\text{dim}}^{\text{solv}} = \Delta S_{\text{dim}} - \Delta S_{\text{dim}}^{\text{tr}}$$

and thus:

$$\Delta H_{\text{dim}}^{\text{solv}} = (\Delta H_{\text{g}\rightarrow\text{s}}/\Delta S_{\text{g}\rightarrow\text{s}}) \Delta S_{\text{dim}}^{\text{solv}}$$

taking for the term within the parentheses the average value given in Table 2.

The  $\Delta H_{\text{dim}}^{\text{solv}}$  values thus found range from  $-40$  to  $-30$  kcal mol $^{-1}$  (Table 3) and can thus compensate, or even overcompensate, the coulombic repulsion. Recalling that  $\Delta H_{\text{dim}}^{\#,\text{rep}}$  and  $\Delta H_{\text{dim}}^{\#,\text{solv}}$  are close to  $\Delta H_{\text{dim}}^{\text{rep}}$  and  $\Delta H_{\text{dim}}^{\text{solv}}$ , respectively, it follows that coulombic repulsion tends to be compen-

sated by increased solvation in the transition state leading to a small, possibly zero, activation enthalpy.

An approximate estimate of the location of the center of negative charge on each monomeric moiety in the dimer dianion (this should be approximately the same for the transition state) can be arrived at as follows,  $r_1$  and  $r_2$  being the radii of the solvation equivalent spheres of the anion radical and for each anionic moiety in the dimer, respectively:

$$\frac{1}{r_2} - \frac{1}{r_1} = \frac{\Delta G_{\text{solv}}^{298}}{2(r\Delta G_{\text{g}\rightarrow\text{s}}^{298})} \quad (2)$$

Table 2. Solvation thermodynamics of anions.<sup>a,b</sup>

Solvent	Anions	Cl $^{-}$	Br $^{-}$	I $^{-}$	ClO $_4^{-}$	
	$\Delta H_{\text{g}\rightarrow\text{w}}$	-81.3	-77.9	-64.1	-58.8	
	$\Delta S_{\text{g}\rightarrow\text{w}}$	-18.2	-14.5	-9.0	-13.6	
	$r^c$	1.81	1.95	2.16	2.92	
DMF	$\Delta H_{\text{w}\rightarrow\text{s}}$	4.3	0.1	-3.6	-5.6	
	$\Delta S_{\text{w}\rightarrow\text{s}}$	-23.7	-25.3	-28.4	-23.9	
	$\Delta H_{\text{g}\rightarrow\text{s}}$	-77.0	-77.8	-67.7	-60.4	
	$\Delta S_{\text{g}\rightarrow\text{s}}$	-41.9	-38.9	-37.4	-37.5	
	$\Delta G_{\text{g}\rightarrow\text{s}}^{298}$	-64.5	-66.2	-56.6	-49.2	
	$\Delta H_{\text{g}\rightarrow\text{s}}/\Delta S_{\text{g}\rightarrow\text{s}}$	1.84	2.00	1.81	1.61	Average 1.81 ( $\pm 9\%$ )
	$-r \Delta G_{\text{g}\rightarrow\text{s}}^{298}$	116.8	129.1	122.2	143.7	128 ( $\pm 9\%$ )
Me $_2$ SO	$\Delta H_{\text{w}\rightarrow\text{s}}$	4.8	1.1	-2.7	-4.3	
	$\Delta S_{\text{w}\rightarrow\text{s}}$	-14.8	-19.4	-20.6	-16.5	
	$\Delta H_{\text{g}\rightarrow\text{s}}$	-76.5	-76.8	-66.8	-63.1	
	$\Delta S_{\text{g}\rightarrow\text{s}}$	-33.0	-33.9	-29.6	-30.1	
	$\Delta G_{\text{g}\rightarrow\text{s}}^{298}$	-66.7	-66.7	-58.0	-54.1	
	$\Delta H_{\text{g}\rightarrow\text{s}}/\Delta S_{\text{g}\rightarrow\text{s}}$	2.32	2.27	2.26	2.10	Average 2.23 ( $\pm 4\%$ )
	$-r \Delta G_{\text{g}\rightarrow\text{s}}^{298}$	123.3	130.1	125.2	158.1	134 ( $\pm 12\%$ )
MeCN	$\Delta H_{\text{w}\rightarrow\text{s}}$	4.6	1.9	-1.8	-4.1	
	$\Delta S_{\text{w}\rightarrow\text{s}}$	-17.7	-18.2	-20.3	-17.2	
	$\Delta H_{\text{g}\rightarrow\text{s}}$	-76.7	-76.0	-65.9	-62.9	
	$\Delta S_{\text{g}\rightarrow\text{s}}$	-35.9	-32.7	-29.3	-30.8	
	$\Delta G_{\text{g}\rightarrow\text{s}}^{298}$	-66.0	-66.3	-57.2	-53.7	
	$\Delta H_{\text{g}\rightarrow\text{s}}/\Delta S_{\text{g}\rightarrow\text{s}}$	2.14	2.33	2.25	2.04	Average 2.18 ( $\pm 6\%$ )
	$-r \Delta G_{\text{g}\rightarrow\text{s}}^{298}$	119.5	129.2	123.5	156.8	132 ( $\pm 13\%$ )

<sup>a</sup>g $\rightarrow$ w: transfer from gas to water, w $\rightarrow$ s: from water to the solvent.  $\Delta H$ ,  $\Delta G$  in kcal mol $^{-1}$ ,  $\Delta S$  in eu. <sup>b</sup>From Refs. 9–12. <sup>c</sup>Radius in Å.

Table 3. Estimation of the contribution of coulombic repulsion and solvation to the reaction enthalpy.<sup>a</sup>

Solvent	$\Delta S_{\text{solv}}$	$\Delta H_{\text{solv}}$	$\Delta G_{\text{solv}}^{\text{Coul}}$	$1/r_2 - 1/r_1$	$r_2$	$d$	$\Delta H_{\text{rep}}$	$\Delta H_{\text{rep}} + \Delta H_{\text{solv}}$
DMF	-21.4	-38.7	-32.4	0.126	2.74	9.13	36.4	-2.4
Me <sub>2</sub> SO	-14.4	-32.1	-27.8	0.104	2.92	8.77	37.8	5.7
MeCN	-19.4	-42.3	-36.5	0.138	2.66	9.30	35.7	-6.6

<sup>a</sup>Units as in Tables 1 and 2.

the term within the parentheses being the average value given in Table 2. This provides an estimate of the displacement of the center of negative charge toward the nitrogen atom on going from the initial anion radical to the dimer dianion. In the former, the center of negative charge is located somewhere between the center of the central benzene ring and the nitrogen atom. If we assume that the charge distribution is similar to that of the 9-chloroanthracene anion radical,<sup>13</sup> the center of charge is located approximately at the 9-carbon, corresponding to  $r_1 = 4.2 \text{ \AA}$  (Fig. 2). The term  $r_1$  is then derived from eqn. (2). As seen in Table 3, its value does not vary very much from one solvent to another. The location of the centers of charge is then deduced from  $r_1$  (Fig. 1) leading, finally, to the repulsion reaction enthalpy,  $\Delta H_{\text{solv}}^{\text{rep}}$  [eqn. (1)]. Although this estimate is rather crude,  $\Delta H_{\text{rep}}^{\text{solv}}$  values thus obtained are certainly closer to reality than the somewhat smaller value previously derived based on the assumption that all the negative charge is located on the nitrile nitrogen.

We thus find (Table 3) that  $\Delta H_{\text{dim}}^{\text{rep}}$  and  $\Delta H_{\text{dim}}^{\text{solv}}$  closely compensate each other. It follows that since

$$\Delta H_{\text{dim}}^{\ddagger} \approx \Delta H_{\text{dim}}^{\text{rep}} + \Delta H_{\text{dim}}^{\text{solv}},$$

$\Delta H_{\text{dim}}^{\ddagger}$  is close to zero, leading to the conclusion that the one-step mechanism model of the dimerization of 9-anthracene anion radicals is perfectly compatible with the experimental data. The contention that 'evidence for the two-step mechanism appears to be indisputable'<sup>7</sup> is therefore far from being 'indisputable'.

Another consequence of the mutual compensation of  $\Delta H_{\text{dim}}^{\text{rep}}$  and  $\Delta H_{\text{dim}}^{\text{solv}}$  is that the dimerization enthalpy is an approximate measure of the strength of the dimer  $\sigma$ -bond in the gas phase, ignoring the coulombic repulsion. The value thus found,  $13 \text{ kcal mol}^{-1}$  could, at first sight, appear

rather small for a carbon-carbon bond. It should, however, be borne in mind that the radical is strongly stabilized by the double benzylic structure of its main resonance form and, furthermore, by its aromatic character.

We also note that the recent finding of a linear correlation between  $\Delta G_{\text{diss}}^{\ddagger}$  and the Gutman acceptor number of the solvent<sup>7</sup> does not provide more evidence for the two-step than for the one-step mechanism. The overall variation of  $\Delta G_{\text{diss}}^{\ddagger}$  is very small (0.8 kcal at 298 K). The correlation indicates that  $\Delta G_{\text{dim}}^{\ddagger, \text{solv}}$  (fraction of the dimerization activation free energy corresponding to the increase of solvation upon going from the initial state to the transition state) is slightly smaller than  $\Delta G_{\text{dim}}^{\text{solv}}$ . This falls in line with the concentration of negative charge being slightly smaller, as

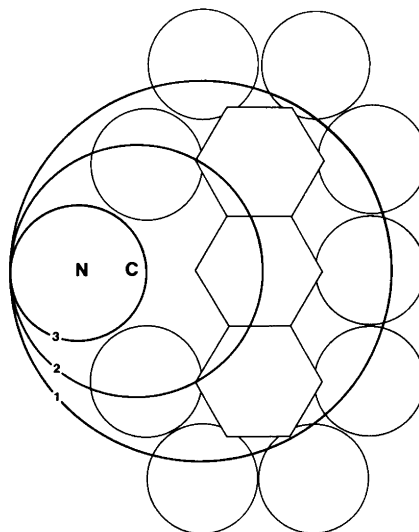


Fig. 2. Equivalent solvation spheres of the anion radical (a) and of each monomeric moiety in the dimer dianion (the bond lengths and Van der Waals radii are taken from Ref. 13).

seems reasonable, in the transition state than in the final state. The fact that a better linear correlation is found with  $\Delta G_{\text{diss}}^\ddagger$  than with  $\Delta H_{\text{diss}}^\ddagger$  or  $\Delta S_{\text{diss}}^\ddagger$  is not surprising since acceptor numbers are themselves based on reaction free enthalpies.

Having reached the conclusion that the one-step mechanism is perfectly compatible with the experimental data, it remains to be discussed whether or not a ' $\pi$  complex' between the two anion radicals could be an intermediate in the dimerization process. Let us examine the possibility for this ' $\pi$  complex' to have a negative enthalpy of formation from the initial anion radicals that would compensate the activation enthalpy supposedly required to form the  $\sigma$ -bond, a central point in advocating the two-step mechanisms.<sup>5</sup> Recent gas-phase molecular-beam studies<sup>14,15</sup> and theoretical calculations<sup>14-17</sup> of sandwich (Van der Waals) dimers of aromatic molecules point to a face-to-face geometry, with a distance of 4-5 Å between the two aromatic rings and an energy of formation of 3-4 kcal mol<sup>-1</sup>. The formation of such ' $\pi$  complexes' requires that the main electronic characteristics of the monomer be retained in the sandwich dimer. Applying these results to the present case indicates a distance between the centers of negative charge of about 6 Å, leading to a coulombic repulsion energy of ca. 55 kcal mol<sup>-1</sup>. On the other hand, since the electronic characteristics of the anion radical are retained in the ' $\pi$  complex' there should not be any significant solvation stabilization by means of charge concentration. It follows that the formation of the ' $\pi$  complex' would involve a substantial *positive* enthalpy (ca. 50 kcal mol<sup>-1</sup>). The aforementioned results concern benzene and substituted benzenes. The reaction might be more exothermic with anthracenes and, at the same time, the distance between the rings smaller. Even if  $\Delta H_1$  is three times that of benzenes, which appears to be a maximum estimate, and even neglecting the increase of coulombic repulsion resulting from a shorter ring distance (5 Å give rise to a 66 kcal mol<sup>-1</sup> repulsion) we see that the formation of sandwich dimer is very unlikely to be exothermic. One could argue that solvent molecules might penetrate the gap in between the two aromatic rings in the sandwich dimer, thus considerably decreasing the coulombic repulsion. However, this will also annihilate the attractive forces between the rings. From a free enthalpy standpoint, the ' $\pi$  complex' is un-

likely to be more stable than the transition state depicted in the above discussion since the attractive forces between the rings are insufficient to compensate for the negative free energy,  $\Delta G_{\text{dim}}^{\ddagger, \text{solv}}$ , corresponding to the increased solvation of the transition state as compared with the initial state (this is of the order of -30 kcal mol<sup>-1</sup>) as discussed earlier.

Our final conclusion is that in the dimerization of 9-cyanoanthracene anion radicals, the one-step mechanism involving the direct formation of the  $\sigma$ -bond is much more likely to take place than a two-step mechanism going through the prior formation of a ' $\pi$  complex'.

Another anthracene anion radical substituted by an electron-withdrawing group, namely 9-nitroanthracene, exhibits behavior quite similar to that of 9-cyanoanthracene<sup>5</sup> which can be interpreted along the same lines as discussed above. However, anion radicals of anthracene itself appear to be perfectly stable toward dimerization. Why does this difference exist? An obvious reason may be that the strength of the  $\sigma$ -bond would change as a function of the 9-substituent. However, factors related to the charge distribution are certainly also involved: in the absence of an electron-withdrawing group able to accommodate a large fraction of the negative charge, coulombic repulsion will be stronger and the increase in solvation from the initial two anion radicals to the transition state or to the dimer dianion weaker - two further reasons for a decreased driving force for dimerization.

*Acknowledgements.* J. P. Morel (*Université de Clermont-Ferrand*) is thanked for helpful advice in the search for reliable data concerning the solvation thermodynamics of anions in non-aqueous solvents. I am indebted to F. Lahmani (*Université de Paris-Sud, Orsay*) for the communication, prior to publication, of her results on the formation of sandwich dimers between aromatic molecules, and for helpful discussions on the matter.

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Received July 4, 1988.