129. The Unexpectedly Stable Dianion of a Naphthalene-Tolan Photoadduct

by **Klaus Müllen**

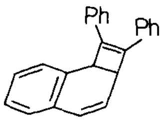
Laboratorium für Organische Chemie der Eidg. Technischen Hochschule
CH-8092 Zürich

(29.XII.77)

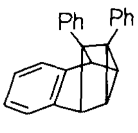
Summary

Metal reduction of the polycycle **2** yields a surprisingly stable dianion with intact molecular framework. This conclusion can be drawn from reoxidation experiments and from an analysis of the ^{1}H-NMR. spectrum. The excess charge turns out to be distributed over both the π- and σ-fragments of the molecule. The relative stabilities of ionic species derived from **1**, **2** and **3** are considered.

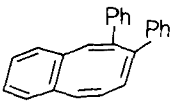
1. Introduction. - It has been described by *Sasse et al.* some time ago that the photochemical addition of tolan (diphenylacetylene) to naphthalene yields the cyclobutene derivative **1** [1]. Compound **1**, however, is not photostable but undergoes an intramolecular $[_\pi 2+_\pi 2]$-cycloaddition resulting in the formation of the polycycle **2**. Thermolysis of **2** affords a mixture of **1** and the ring opened cyclooctatetraene derivative **3**.



1



2



3

We attempted to convert **1** and **2** into their radical anions and dianions with two main points in mind:

1) does the presence of a negative charge influence the isomerization processes and

2) what is the relative stability of the isomeric anions depending on the charge distribution adopted?

The first question was suggested by the well documented result [2] [3] that the energy of activation of pericyclic reactions can be significantly lowered when transforming a molecule into its radical anion. Concerning question 2 one usually explains the stability of anions derived from fully unsaturated molecules by the existence of extended charge delocalization within the entire π-system. Surprisingly enough the dianion $\mathbf{2}^{--}$ turns out to be stable, and we show below that the extra charges are delocalized over both the π- and σ-fragments of the molecule.

2. Experimental and results. - On reduction with potassium in tetrahydrofuran (THF) at $-78°$ compound **1** forms a radical anion which can be detected by means of its ESR. and ENDOR. spectrum[1]. Above $-40°$ the ESR. signal of $\mathbf{1}^{\dot{-}}$ is slowly replaced by that of the *trans*-stilbene radical anion. Reducing compound **2** at $-78°$ with potassium or sodium in tetrahydrofuran, 2-methyltetrahydrofuran or dimethoxyethane produces exclusively the naphthalene radical anion identified by its ESR. signal. On warming the solution one records the ESR. spectrum of the *trans*-stilbene radical anion. By contacting a solution of **2** in THF at *ca.* $-90°$ with potassium one also succeeds in detecting the tolan radical anion.

Assuming that the radical anion of *trans*-stilbene is formed *via* the tolan radical anion [5] the identification of the above radical anions clearly indicates the occurrence of fragmentation reactions in both $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{\dot{-}}$: the radical anion $\mathbf{1}^{\dot{-}}$, in contrast to the neutral compound, undergoes a $[_{\sigma}2+_{\sigma}2]$-cycloreversion with cleavage of the 4-membered ring. Consequently, no rearrangement occurs to the cyclooctatetraene derivative $\mathbf{3}^{\dot{-}}$ which as a disrotatory ring opening of the cyclobutene fragment might be favoured by generation of the radical anion [2]. It remains uncertain, however, whether the radical anion $\mathbf{2}^{\dot{-}}$ decomposes *via* formation of the isomer $\mathbf{1}^{\dot{-}}$ or *via* a simultaneous cleavage of four σ-bonds[2].

Reduction of **2** with lithium (THF, $-78°$) produces a radical anion which can be detected by its rather weak and poorly resolved ESR. spectrum. No cleavage reactions are observed under these conditions. Further metal contact, however, causes the ESR. signal to disappear. These findings, namely the importance of the counterions for the stability of the anions, warranted a detailed investigation of the lithium reduction of **1** and **2**.

Bringing compound **1** or **2**, in THF-d_8 (*ca.* $5 \cdot 10^{-2}$M) at $-78°$, into contact with lithium for prolonged periods of time affords deep red brown and rust brown solutions, respectively. The failure to observe an ESR. signal at the end of the reduction indicates the absence of any radical anions. The ^{1}H-NMR. spectra taken at this stage show no trace of the starting materials. Reoxidation of the reduction product with dry oxygen at $-78°$, in the case of **2**, yields the starting material (+polymer), in the case of **1**, however, one recovers a complex mixture of unidentified products which contains no starting compound and only traces of naphthalene and tolan (as detected by GC.-analysis). These results point towards the surprising fact that compound **2** on reduction transforms to a diamagnetic dianionic species, $\mathbf{2}^{--}$, in which the molecular framework of the starting compound is

---

[1] The ^{1}H-hyperfine coupling constants extracted from the ENDOR. spectrum of $\mathbf{1}^{\dot{-}}$ are 0.25, 0.50, 0.71, 2.21, 2.50, 2.88, 3.82, 4.14, and 6.30 Gauss, respectively. A detailed analysis of these data demonstrating the spin density to be essentially localized in the stilbene moiety will be published elsewhere [4].

[2] That one obtains the stable fission products (*e.g.* the naphthalene radical anion) directly might favour the latter assumption. The identification of the secondary radical anions, however, appears to be sensitive to the particular conditions of the reduction.

preserved. The formation of a dianionic cyclooctatetraene species **3**$^{--}$ which one might expect to constitute the favourable form of the three isomeric dianions can therefore be excluded. A detailed analysis of the ^{1}H-NMR. spectrum of **2**$^{--}$ (see below) provides firm evidence in favour of the proposed structural assignment.

The dianion **1**$^{--}$ turns out not to be stable but suffers, as can be deduced from the highly increased intensity of aliphatic signals, from protonation reactions.

3. Discussion. - In *Figure 1* are compared the ^{1}H-NMR. spectra of the neutral compound **2** and of the corresponding reduction product. In particular the spectrum presented in *Figure 1c* is ascribed to the dianion **2**$^{--}$. Based on the relative signal intensities and on the observed coupling patterns (as clarified by decoupling experiments, see *Figure 1d* and *1e*) in this spectrum we succeeded in identifying the ^{1}H-resonance signals of the two phenyl substituents, of the ortho-disubstituted benzene fragment and of the 'aliphatic' part. Setting the decoupling frequency at the signal of protons H–C(4) (H–C(3)), H–C(5) and H–C(6) causes the resonance signals of H–C(3)(H–C(4)), and H–C(7), respectively, to collapse into singlets. Likewise, during irradiation at the resonance frequency of H–C(6′), the nuclei H–C(5′) and H–C(7′) give rise to sharp singlet signals. It is therefore possible to identify the resonances of ortho-, meta- and para-protons within both phenyl groups, but it is not possible from experimental evidence to differentiate between the individual phenyl rings. As a whole, these data are consistent with a molecular structure which is identical with that of the neutral species.

The ^{1}H-NMR. spectrum of the dianion **2**$^{--}$ exhibits normal linewidths. This confirms the absence of paramagnetic material. It is, however, somewhat surprising that no significant line broadening can be observed in the ^{1}H-NMR. spectrum which is taken in the course of the reduction (see *Fig. 1b*). A comparison of *Figures 1a, 1b* and *1c* reveals that the 'intermediate' spectrum shows relatively sharp signals of both the neutral and dianionic species. This result indicates that the concentration of the initially formed radical anion remains very low throughout the reduction (which finding might also be deduced from the weak ESR. signal) and that no fast electron exchange between the neutral and ionic species occurs.

Comparing the proton chemical shifts of the dianion **2**$^{--}$ with those of the neutral compound (see *Table*) demonstrates that the signals not only of aromatic (H–C(3), H–C(4), H–C(5)–H–C(7), H–C(5′)–H–C(7′)) but also of aliphatic

Table. *^{1}H-NMR. chemical shifts*[a]) *for the neutral molecule* **2** *and its corresponding dianion* **2**$^{--}$

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H–C(7)	H–C(5′)	H–C(6′)	H–C(7′)
τ(**2**)	7.42	5.64	2.91	2.91	2.91	2.91	2.91	2.91	2.91	2.91
τ(**2**$^{--}$)	9.28[b])	6.65[b])	3.33[c])	3.62[c])	3.62[d])	3.62	4.34	4.59	4.07	5.37
$\Delta\tau$[(**2**$^{--}$)-(**2**)]	1.86	1.01	0.42	0.71	0.71	0.71	1.43	1.68	1.16	2.46

[a]) Chemical shifts are given in τ [ppm]. They have been measured with respect to the solvent resonances (tetrahydrofuran-d_8, – 80°) and then referred to TMS.

[b]) This signal assignment has been made in analogy with the one in the neutral compound.

[c]) The relative assignment of H–C(3) and H–C(4) is tentative.

[d]) No differentiation is possible between the two phenyl groups.

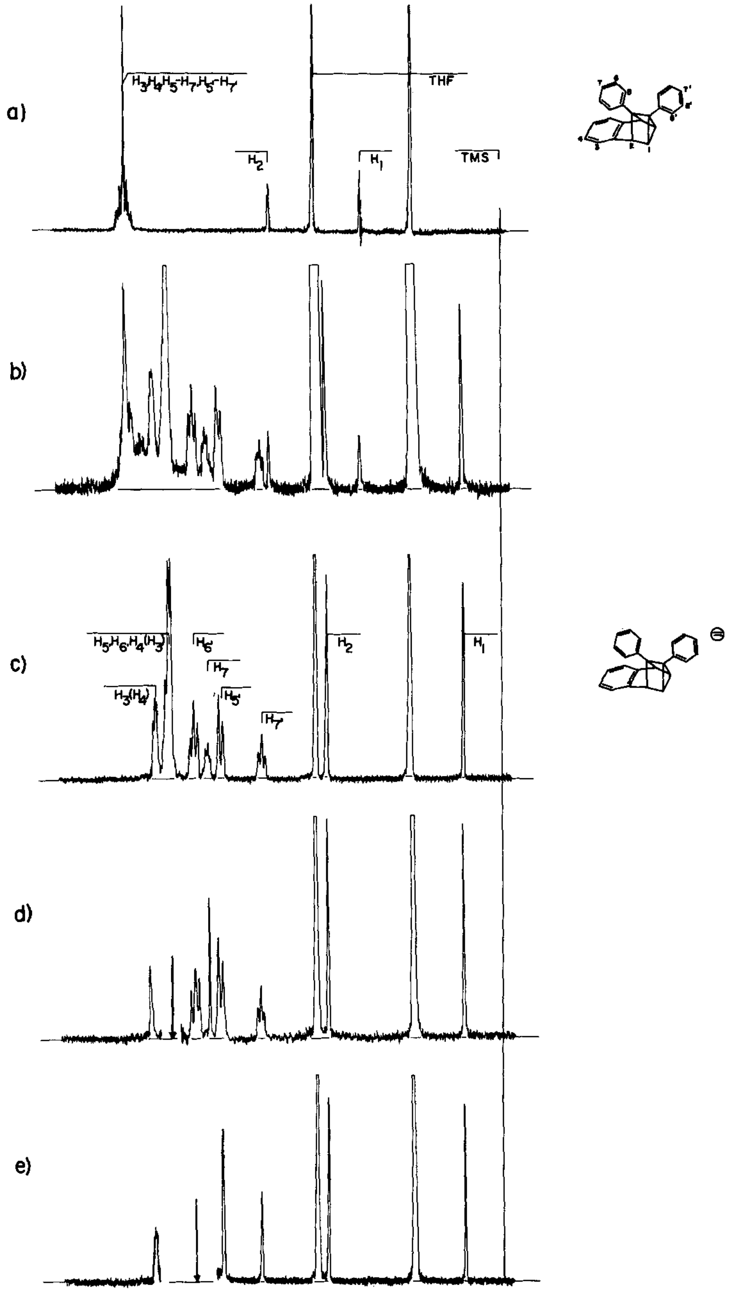


Figure. ^{1}*H-NMR. spectra* (100 MHz, CW-mode; THF-d_8; −80°)
1a) ^{1}H-NMR. spectrum of the neutral polycycle **2**. 1b) 'Intermediate' spectrum recorded during the metal reduction of **2**, see text. 1c) ^{1}H-NMR. spectrum of the dianion (2^{--}) (as lithium salt) recorded after complete reduction. 1d, e) Decoupling experiments for the dianion 2^{--}, the irradiation frequencies are indicated by arrows.

protons (H-1, H-2) exhibit a distinct upfield shift. From the well established proportionality between chemical shifts and the corresponding charge densities [6] one can conclude that the extra charges in **2**$^{--}$ are delocalized over the entire molecule, *i.e.* π- as well as σ-fragments.

In considering this bonding situation it is useful to compare the isomers **1** and **2**. As has been pointed out compound **1** does not form a stable dianion. The dianion resulting from reduction of **2**, however, appeared to be fairly stable even at room temperature. Bearing in mind that in **1**$^{--}$ a conjugative interaction between the stilbene moiety and the rest of the molecule would be prohibited for steric reasons one might well deduce that the occurrence of charge delocalization in the dianion **2**$^{--}$ is due to the relative orientation of π- and σ-orbitals. In **2** the 'pseudo'-p_π-functions resulting from linear combination of the relevant C,C-σ-bonds between the aliphatic centers seem to be properly oriented for interaction with the neighbouring π-orbitals. On the other hand, the stability of the ionic species mentioned herein strongly depends on the nature of the counterion. One might therefore also assume the charge delocalization in **2**$^{--}$ to be significantly influenced by the specific association within the ion pair.

Financial support of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (project 2.747/0.77) is gratefully acknowledged.

REFERENCES

[1] *P.J. Collin & W.H.F. Sasse,* Tetrahedron Letters *1968,* 1689; *C. Kowala, B.J. Poppleton & W.H.F. Sasse,* Austral. J. Chemistry *29,* 1851 (1976).

[2] *S.F. Nelsen & J.P. Gillespie,* J. Amer. chem. Soc. *95,* 2940 (1973); J. org. Chemistry *38,* 3592 (1973).

[3] *J.R. Dodd, R.F. Winton, R.M. Pagni, C.R. Watson jr. & J. Bloor,* J. Amer. chem. Soc. *96,* 7846 (1974).

[4] *W. Huber & K. Müllen,* to be published.

[5] *G. Levin, J. Jagur-Grodzinski & M. Szwarc,* J. Amer. chem. Soc. *98,* 2268 (1970).

[6] *T. Schaefer & W.G. Schneider,* Canad. J. Chemistry *41,* 966 (1963); *H. Spiesecke & W.G. Schneider,* Tetrahedron Letters *1961,* 468.