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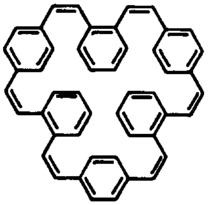
A SIXFOLD TRIPLET-SENSITIZED *Z*/*E* ISOMERIZATION OF A π-PERIMETER MACROCYCLE

Mikael Sundahl[a], Olof Wennerström*[a], Kjell Sandros[b] and Ulf Norinder[a]

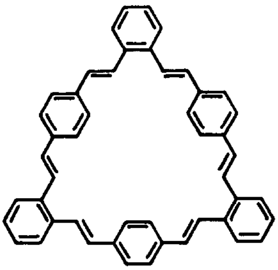
Departments of Organic[a] and Physical[b] Chemistry, Chalmers University
of Technology, S-412 96 Göteborg, Sweden

Abstract. On irradiation, all-*Z* [2.2.2.2.2.2]orthoparacyclophene (**1**) is converted to the all-*E* isomer (**2**). The photo-isomerization occurs *via* the triplet state and proceeds without any ground state intermediates.

Theoretical and experimental studies of photo-induced *Z*/*E* isomerization in linear polyenes and α,ω-diphenylpolyenes (stilbene in particular) are numerous[1]. However, our knowledge of such isomerizations in macrocyclic π-systems is limited. In the larger annulenes, for example, facile valence isomerizations are usually possible[2] and these prevent the study of any photo-induced isomerizations. The presence of local aromatic rings in the macrocycle as well as a certain ring size seem to be necessary conditions for the experimental observation of *Z*/*E* isomerizations in large cyclic π-systems and cyclophenes of proper ring size have now become available.[3] We recently proposed that the photo-isomerization of [2.2.2.2.2.2]paracyclophenes, which involves more than one double bond, occurs without ground state intermediates.[4] In this paper we present evidence for the sixfold isomerization of a closely related macrocycle, all-*Z* [2.2.2.2.2.2]orthoparacyclophene (**1**) to the all-*E* isomer (**2**).

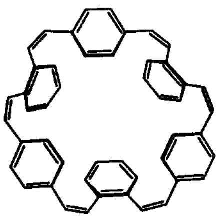


1

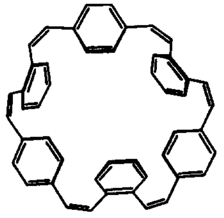


2

The synthesis of (1) by a stereoselective sixfold Wittig reaction between benzene-1,2-dialdehyde and the bisphosphonium salt from 1,4-bis(bromomethyl)-benzene has been reported elsewhere.[5] From a DNMR study we concluded that (1) exists in solution as a mixture of two conformational isomers (1A) and (1B) which interconvert rapidly on the NMR-time scale at ambient temperature.[6] Conformer (1A) has a bowl-shaped structure (approaching C_{3v}-symmetry) whereas (1B) is less symmetric (approaching C_s-symmetry) as shown by molecular mechanics calculation (Allinger's MMP2 force field)[7] and inspection of CPK-models.



1A



1B

Upon irradiation (300 nm, benzene or chloroform), cyclophene (1) is smoothly converted to (2), the structure of which follows from the ^{1}H NMR spectrum as well as from MS, UV- and IR-data [NMR and UV are shown in Fig. 1. IR: 955(s), 800(s), 740(s) cm^{-1}. MS: *m/e* 612(M$^+$). M.p. >370 (decomp.)]

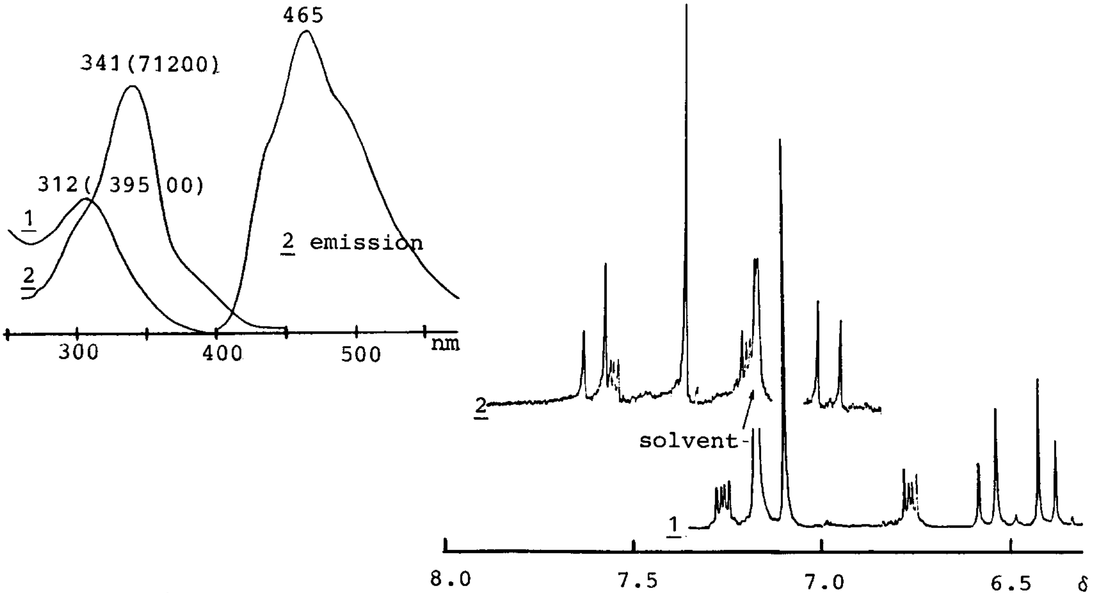


Figure 1. ^{1}H NMR (270 MHz, C_6D_6) and UV (cyclohexane) spectra of all-*Z* (1) and all-*E* (2) [2.2.2.2.2.2]orthoparacyclophene. The fluorescence spectrum of the all-*E* isomer is also shown.

In principle there are many possible routes from (1) to (2), the two extremes being the direct interconversion whithout any ground state intermediates and the stepwise process in which one Z-double is isomerized in each photo-reaction. The latter case is shown in Figure 2.

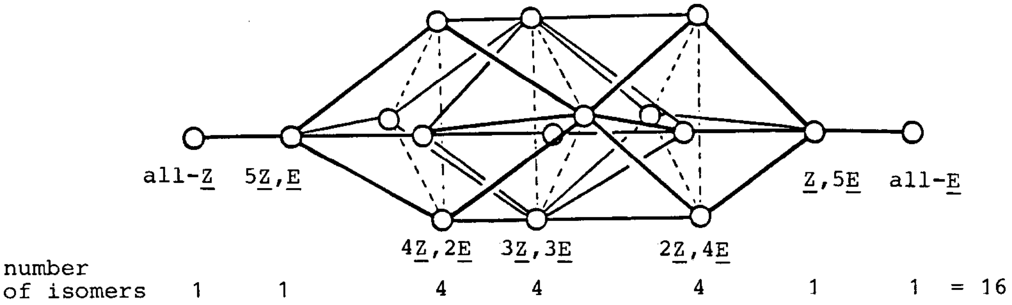


Figure 2. A graphical representation of the stepwise isomerization of all-Z to all-E [2.2.2.2.2.2]orthoparacyclophene with all possible Z/E isomers as intermediates. Circles (o) represent configurational isomers (16) and the solid lines show the possible isomerizations.

The photoisomerization of (1) to (2) was followed by ^{1}H NMR spectroscopy. No intermediates were observed (<5%). Cyclophene (2), in contrast to (1), shows a strong fluorescence (Fig. 1) and the fluorescence spectrum of the reaction mixture at different degrees of conversion showed (2) to be the only fluorescent compound present. The quantum yield for the conversion of (1) to (2) at 305 nm was calculated to 2.7% (ferrioxalate actinometer and UV-spectroscopical analysis). These results indicate that a direct conversion is probable, but a stepwise process can not be rigorously ruled out.

Conclusive evidence for the direct photoisomerization came from an experiment with biacetyl as a sensitizer. Cyclophene (1) was dissolved in benzene with and without addition of biacetyl. The two samples were sealed off under a good vacuum and irradiated, the reactions being followed by ^{1}H NMR spectroscopy. Irradiation of the samples at >400 nm resulted in a rapid isomerization of the biacetyl-containing sample and virtually no isomerization of the other sample. If the latter was irradiated at 300 nm isomerization was then observed but at a slower rate. The same result was obtained by UV-spectroscopy and the quantum yield for the sensitized reaction was calculated to 62% (λ_{exc}= 436 nm). Assuming the same rate constant for triplet energy transfer to (1) and (2) a constant quantum yield was obtained in the conversion range 0-0.8. Thus, little doubt remains that the photo-isomerization of (1) to (2) is a direct sixfold process occurring in the triplet state.

Since it is generally observed that E-isomers are thermodynamically more stable than the corresponding Z-isomers, the formation of (2) from (1) must be an exothermic reaction. Cyclophene (2) can attain an almost planar conformation with minimal steric congestion of the inner olefinic hydrogens whereas (1) is non-planar with considerable steric strain in both low-energy conformers (1A) and (1B). Molecular mechanics calculations place both (1A) and (1B) more than 40 kcal mole^{-1} above (2). The simple assumption that the relative triplet energies parallel the singlet ones then leads to the conclusion that the formation of (2) from (1) on the triplet surface releases 40-50 kcal mol^{-1}. As only one product is observed, very little information on the triplet energy surface is available. In contrast, the isomerization of [2.2.2.2.2.2]paracyclophenes can be initiated from several different ground state isomers and two different isomers are formed on irradiation.[4]

It is remarkable that in spite of the relatively inefficient unsensitized conversion of (1) to (2), no clear evidence for the formation of dehydrophenanthrene or phenanthrene derivatives has been observed, and only few examples of this type of reaction are known for π-perimeter cyclophenes in general. Available data thus indicate that the photochemistry of π-perimeter macrocycles is very different from that of the open chain counterparts. Although π-perimeter cyclophenes in the ground state should be regarded as normal aromatic compounds with no measurable effect of the formal π-perimeter, a number of the corresponding anions are known to be annulene-like.[8] Further work on the photochemistry of such cyclophenes will hopefully reveal the major factors responsible for their excited state properties and reactions.

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References

1. Houben-Weyl "Methoden der Organischen Chemie" Band 4, Teil 5a, G. Thieme Verlag, Stuttgart 1975, p. 184-212; Kushick, I.N., Rice, S.A. J. Chem. Phys. 1976, 64, 1612; Taran, P., Schulten, K. Chem. Phys. Lett. 1978, 56, 200; Ohmine, I., Morokuma, K. J. Chem. Phys. 1980, 73, 1907; Said, M., Maynav, D., Malrieu, J.-P. J. Am. Chem. Soc. 1984, 106, 580.
2. Oth, J.F.M. Pure Appl. Chem. 1971, 25, 573; Sondheimer, F. Acc. Chem. Res. 1972, 5, 81; Farell, L., Kao, J., Radom, L., Schaefer, H.F. J. Am. Chem. Soc. 1981, 103, 2147; Günther, H., Schmickler, H., Königshofen, H., Recker, K., Vogel, E. Angew. Chem. 1973, 85, 261; Otsubo, T., Gray, R., Boekelheide, V. J. Am. Chem. Soc. 1978, 100, 2449.
3. Raston, I., Wennerström, O. Acta Chem. Scand. 1982, B36, 655.
4. Norinder, U., Tanner, D., Wennerström, O. Tetrahedron Lett. 1983, 5411.
5. Thulin, B., Wennerström, O., Somfai, I. Acta Chem. Scand. 1978, B32, 109.
6. Olsson, T., Tanner, D., Thulin, B., Wennerström, O. Tetrahedron 1981, 37, 3491.
7. Burkert, U., Allinger, N.L. "Molecular Mechanics", ACS Monograph 1982, 177.
8. Müllen, K., Unterberg, H., Huber, W., Wennerström, O., Norinder, U., Tanner, D., Thulin, B. J. Am. Chem. Soc. 1984, 106, 7514.

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