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Journal of Photochemistry and Photobiology A: Chemistry 105 (1997) 205–207

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Stereoisomerism of 4a,4b-dihydrophenanthrenes [1]

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Received 11 September 1996; accepted 12 September 1996

Abstract

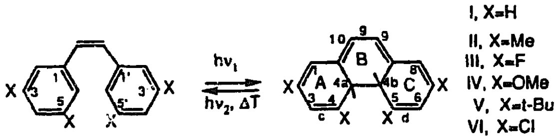
We reported previously that sterically hindered photochromic 4a,4b-dihydrophenanthrenes can exist in two modifications. These labile intermediates are designated as L (long) or S (short) according to the position of their visible absorption band. We presently suggest that these are two conformers ap (L) and ac (S) of the central C(4a)–C(4b) ethane unit. ap is the more planar while ac is decidedly distorted. Spectral characteristics—the position and intensity of the visible absorption band—provide the basis for the conformation assignment. The relative stabilities of L and S depend on the type and magnitude of the steric interaction X(4)–X(5) vs. X(4)–H(4b)/X(5)–H(4a). © 1997 Elsevier Science S.A.

Keywords: Photocyclization; Photochromism; Photointermediates; 4a,4b-Dihydrophenanthrenes; Labile conformers; Stilbenes

1. Introduction

4a,4b-Dihydrophenanthrenes [2] [1,2] are reactive, labile photointermediates formed by the concerted photocyclization of *cis*-stilbene and other *cis*-1,2-diaryl ethylenes (Scheme 1). The existence of two different modifications of 4a,4b-dihydrophenanthrenes can be observed on the introduction of substituents such as methyl, fluorine, methoxy, *t*-butyl and chlorine at the 4- and 5-positions [8–10], or [c,d] dibenzoannelation in the [c,d] dibenzoannelated 4a,4b-dihydrophenanthrenes [11–13]. The observation of these two modifications is traceable to the steric strain due to such groups.

In this preliminary report, we wish to provide an assignment of the structures of these modifications. This assignment is fully supported by detailed structure–strain energy analyses which will be described in a future publication. The experimental modifications are termed as L and S [12,13], depending on the spectral position (L, long; S, short) of their visible absorption band.



Scheme 1.

2. Results

In the absence of the above-mentioned substituents, both experimental and theoretical results show clearly that 4a,4b-dihydrophenanthrenes exist in a single modification with an antiperiplanar [3] (e.g. trans) conformation of the 4a- and 4b-hydrogenes (Fig. 1(A)) [2,5,6]. This will be denoted as the ap-type conformation. We suggest that the L modifications of strained 4a,4b-dihydrophenanthrenes belong to this conformation.

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[1] Presented at the International Meeting of Physical Chemistry on *Intra- and inter-molecular photoprocesses of conjugated molecules*, Riccione, Italy, July 14–18, 1996.

[2] For a review of 4a,4b-dihydrophenanthrenes, see Ref. [1]. We refer here to the C_2 symmetry species formed by photocyclization, an allowed conrotatory [3] excited state process of a triene-like system. Experimental evidence [1,4,5] clearly indicates an antiperiplanar C_2 symmetry structure. Correlations based on complete MO analyses [6] clearly support this prediction of orbital symmetry conservation rules. The C_2 conformations cannot convert to the hypothetical conformations of C_{2v} symmetry that would be formed had the forbidden disrotatory photocyclization been feasible.

[3] For the nomenclature of ethane conformers, see Rigaudy and Klesney [14]. The antiperiplanar conformation was previously denoted as trans 4a,4b [6]a.

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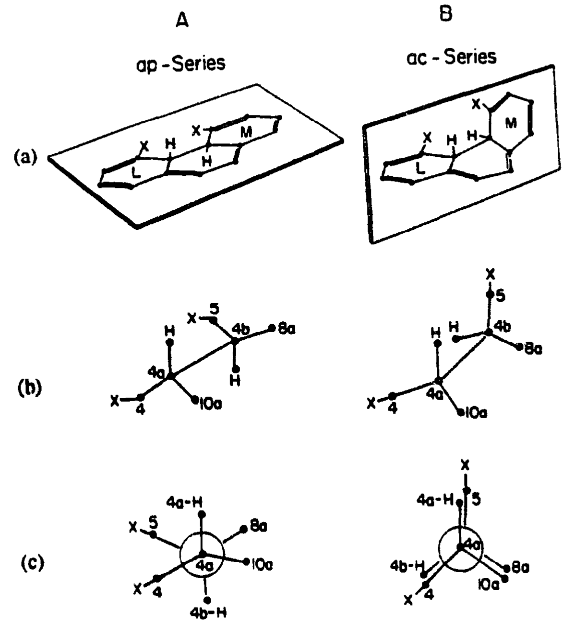

Fig. 1. a. Conformations of 4a,4b-dihydrophenanthrenes: A, antiperiplanar (ap)4a,4b-diH; B, anticlinal, (ac)4a,4b-diH. ap and ac conformations along the 4a,4b C–C single bond are shown in b. Newman projections along this bond are given in c. Note the eclipsed pair of bonds, 4a-H(4a) and 4b-5, of ac 4a,4b-dihydrophenanthrene shown in c.

Members of the S modification are now assigned to the anticlinal, ac-4a,4b-diH conformation of the two hydrogens (Fig. 1B). These molecules are significantly twisted about the 4a–4b bond, and are appreciably less planar than the ap molecules. The orbital symmetry conservation rule applied to the electrocyclic processes of these molecules requires that both conformers belong to the C_2 point group [2–4,6]. The two-fold symmetry axis in the two series passes through the midpoints of the 4a–4b and 9–10 bonds. The transition from the ap to the ac conformation involves a significant torsion about the 4a–4b bond accompanied by torsions about the bonds 1–10a and 8–8a.

Table 1 lists some properties of several L(ap) and S(ac) conformers. The properties of ap-II and ap-V should be compared to those of ap-I and ap-VII ([c,d]dibenzo-II). The structures and conformations of the ap and ac series are closely related, as indicated inter alia by the observed facile conversion of the ap series members of III, IV, and VII to their ac counterparts. In fact, the thermal decay of these stereoisomers takes place by isomerization to the corresponding ac conformer. Because of the very short lifetimes in the ap series (50 μs to 1 s at room temperature, see Table 1), the assignment of the ap conformation to the more labile series currently has to be based on visible spectral evidence such as the dependence of the absorption band intensities and energies on the skeletal conformation (for analyses of the spectral intensities and energies of 4a,4b-dihydrophenanthrenes, see Refs. [1], [2a] and [15]).

Because of their greater departure from planarity, ac conformers should absorb at higher energies than their ap counterparts. This conclusion is borne out by the data of Table 1. For the same reason, the extinction coefficients of the less planar ac conformers should be higher than those of the ap conformers. This somewhat unexpected conclusion is the result of cancelling out in the summation scheme of the one-ethylene unit transition moment vectors for the fundamental transition. The visible transition of I (constrained to the completely planar hexaene structure) has exactly zero intensity. The intensity of this transition can be shown to increase with increasing departure from planarity, going from ap to ac. The experimental data for IV are $\epsilon_L = 4\times10^3$, $\epsilon_S = 9\times10^3$ M^{-1} cm^{-1}.

In the absence of 4,5-disubstitution or [c,d] benzoannelation, ap-4a,4b-dihydrophenanthrenes show a broad visible absorption band (in I, λmax = 450 nm; $\epsilon = 6000$) M^{-1} cm^{-1} [1,2] as well as moderate stability. Thus, in the absence of oxidation, the half-life for the ground state ring opening of I amounts to 90 min at 300 K [1,2].

However, with increasing scope and diversity of the systems investigated, a change in the above uniform pattern could be seen, giving rise to variants of the regular ap-4a,4b-dihydrophenanthrenes which show greatly reduced stability and long wavelength-shifted visible absorption maxima. The primary photocyclization products are now uniformly assigned to the ap conformation [4].

Table 1
Periplanar and anticlinal 4a,4b-dihydrophenanthrenes; stability and absorption data

	4,5-substituent	Antiperiplanar (ap)		Anticlinal (ac)	
		Lifetime	Absorption (nm)	Lifetime	Absorption (nm)
I	H	96 min/298 K	450		
II	CH_3	9 ms/293 K	525		
III	F		480		420
IV	OCH_3	50 μs/300 K	510	50 s/300 K	452
V	*t*-Bu	6 ms/203 K	550		
VI	Cl	4.1 ms/310 K	530		
VII	([c,d]dibenzo-II)	0.4 s/300 K	540	Stable/300 K	460

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[4] Efforts to trap 4a,4b-dihydrophenanthrenes as Diels–Alder adducts have proved unsuccessful. Dienophiles such as maleimide, *N*-phenyl maleimide and maleic anhydride are unreactive at room temperature, while tetracyanoethylene reacts rapidly to give phenanthrene, by abstraction of the 4a and 4b hydrogens.

3. Discussion

The first case to depart significantly from the pattern observed in I was that of 2,4,5,7-tetramethyl-4a,4b-dihydrophenanthrene, reported in 1972 [8]. This photocyclization product of 3,5,3′,5′-tetramethyl stilbene shows exceedingly low stability, undergoing ground state ring opening even at 100 K. Its visible absorption maximum is red shifted to 525 nm [8]. It is now assigned to the ap conformation.

The second exception to the common trend observed in I was found in the photocyclization of 1,2-di(2′-naphthyl) cyclopentene [11]. Here, the observed photoproduct (denoted now as S, completely stable up to 300 K, visible absorption maximum at 430 nm) is actually preceded by a labile stereoisomer (L, lifetime 0.4 s at 300 K, absorption maximum at 490 nm) [11]. S and L are presently assigned respectively to the ac and ap conformations (thus reversing the conclusion of Ref. [11]).

The L modifications of III, IV, V, and VI are all unstable and show a red-shifted visible absorption band [8,9]. The properties of these conformers clearly suggest their assignment to the same ap series.

In III, IV and VII, the L modifications (now concluded to be ap conformers) were shown to be primary low temperature products of photocyclization [9]. At higher temperatures (in III and IV at 193 K), the formation of the labile ap photoproduct is accompanied by that of the more stable S(ac) product. In the case of IV, the ac and ap stereoisomers were shown to be in thermal equilibrium at around 190 K. In the case of III, the ap conformer is converted irreversibly to the ac conformer at temperatures above 120 K when in decalin solution, but the two conformers coexist in equilibrium at 100 K in a methylcyclohexane/2-methylpentane glass. In II, V, and VI, the ap stereoisomers are the only observable photoproducts [8,9].

4. Conclusions

Thus, the strain energies of ap conformers are lower than those of the ac conformers in II, V, and VI. In III and IV, the strain energies of ap and ac conformers are comparable, while in the dibenzoannelated system VII, ac is decidedly more stable than ap [11–13]. This outcome is mainly decided by the interplay of X_4–X_5 vs. X_4–H_{4b}/X_5–H_{4a} interactions.

The ground state ring opening process of ap-4a,4b-dihydrophenanthrenes is forbidden according to the orbital symmetry conservation rules [6], but is observable in practice because of the very high ground state energies of those photoproducts. The same conclusion applies undoubtedly to the ground state ring opening process of the ac-4a,4b-dihydrophenanthrenes.

References

[1] K.A. Muszkat, Top. Curr. Chem., 88 (1980) 89.

[2] (a) K.A. Muszkat and E. Fischer, J. Chem. Soc., (1967) 662.(b) K.A. Muszkat, D. Gegiou and E. Fischer, Chem. Commun., (1965) 447.

[3] R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, 1970.

[4] (a) Th.J.H.M. Cuppen and W.H. Laarhoven, J. Am. Chem. Soc., 94 (1972) 5914.(b) Ch. Goedicke and H. Stegemeyer, Chem. Phys. Lett., 17 (1972) 492.

[5] (a) A. Bromberg and K.A. Muszkat, J. Am. Chem. Soc., 91 (1969) 2860.(b) A. Bromberg, K.A. Muszkat and E. Fischer, Chem. Commun., (1969) 1352.

[6] (a) K.A. Muszkat and W. Schmidt, Helv. Chim. Acta, 54 (1971) 1195.(b) K.A. Muszkat, G. Seger and S. Sharafi-Ozeri, J. Chem. Soc., Faraday Trans. 2, 71 (1975) 1529.(c) K.A. Muszkat and S. Sharafi-Ozeri, Chem. Phys. Lett., 20 (1973) 397.

[8] A. Bromberg, K.A. Muszkat and E. Fischer, Israel J. Chem., 10 (1972) 765.

[9] N. Castel, E. Fischer, J. Rauch, M. Jabalameli and W. Lüttke, J. Photochem. Photobiol. A: Chem., 50 (1989) 221.

[10] K.A. Muszkat, N. Castel, A. Jakob, E. Fischer, W. Lüttke and K. Rauch, J. Photochem. Photobiol. A: Chem., 56 (1991) 219.

[11] T. Wismontski-Knittel, M. Kaganowitch, G. Seger and E. Fischer, Recl. Trav. Chim., 98 (1979) 114.

[12] Y. Ittah, A. Jakob, K.A. Muszkat, N. Castel and E. Fischer, J. Photochem. Photobiol. A: Chem., 56 (1991) 239.

[13] K.A. Muszkat, A. Jakob, N. Castel, E. Fischer, K. Rauch and W. Lüttke, J. Photochem. Photobiol. A: Chem., 60 (1991) 193.

[14] J. Rigaudy and S.P. Klesney, IUPAC Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F, Pergamon, Oxford, 1979. p. 484.

[15] (a) R. Korenstein, K.A. Muszkat and S. Sharafi-Ozeri, J. Am. Chem. Soc., 95 (1973) 6177.(b) K.A. Muszkat, in S. Patai and Z. Rapoport (Eds.), The Chemistry of Quinonoid Compounds, Vol. 2, Part 1, Wiley, Chichester, 1988, pp. 203–224.