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(12) Water plays a fundamental role in the interaction process as no hypochromic effect can be detected in ethanol. Ionic interactions intervene to a fairly small extent, as no dramatic change is observed when the pH is varied; Ade-C_3-Q shows a maximum *H* value (25.5%) under neutral conditions (Ade, neutral; Q, protonated). At pH 1, when both rings are protonated, the hypochromic effect remains large (19.5%).

(13) See ref 5 and 8. The following % *H* values were found by the authors: Ade-C_3-Ade, 14.8; Ade-C_3-Thy, 11.7; Ade-C_3-Gua, 14.9; Ade-C_3-Cyt, 13.9; Gua-C_3-Gua, 15.8.

(14) These results have been confirmed by a preliminary NMR study carried out under the same conditions of solvent, pH, and concentration.

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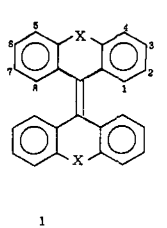
Fast Thermal *Z,E* Isomerization in Symmetrical Overcrowded Ethylenes. Low Barriers Due to Ground-State Destabilization[1]

Sir:

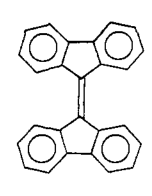
The study of the mechanisms of uncatalyzed thermal *Z,E* isomerizations around carbon–carbon double bonds has been focused mainly on polarized ethylenic systems and on electronic effects.[2,3] Very little attention has been drawn to *Z,E* isomerizations in *symmetrical overcrowded ethylenes*, in which steric effects might become decisive.[2,3] In this series, a dominant role has been played by the bis-tricyclic systems **1**. The strain built in **1**, by the considerable overlap of the van der Waals radii in the region of the central double bond ("pinch"), leads to deviations from planarity and to various distortions, e.g., folding of the benzene rings, and twisting and stretching of the "pinch".[4-6] Fast diastereomerizations were observed in 1,1′-disubstituted $\Delta^{9,9'}$-bisfluorenylidenes carrying bulky groups,[7] but it was not clear whether these exchange processes represented *Z,E* isomerizations or the interconversion between twisted and folded ethylenes of the chiral *E* conformation.[2] In any event, these phenomena are not an intrinsic feature of the bisfluorenylidene system (**2**).[8] We report fast true *Z,E* isomerizations in



1

3. X = C=O

4. X = N–R



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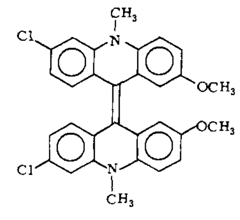
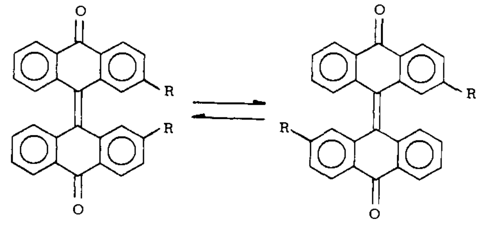


Z - 7

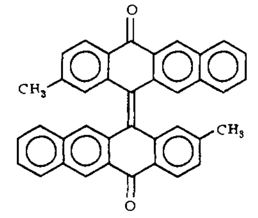


Z - 5, R = CF_3

Z - 6, R = CH_3

E - 5, R = CF_3

E - 6, R = CH_3



E - 8

the bianthrone (**3**) and the biacridan (**4**) series. We ascribe the unusual low energy barriers in these systems predominantly to a destabilization of strained ground-state conformations. Hitherto, the existence of *Z,E* isomers and thermal isomerizations in these series has hardly been established.[9-12] These aspects have been overlooked in the extensive studies of the origin of the photochromic, thermochromic, and piezochromic properties of the bianthrones.[5,9,13-15]

Bianthrone and biacridan derivatives seemed to be promising substrates for the present investigation because of the higher degree of overcrowding (in the ground state planar model) relative to **2**. The following unconventional tailor-made substituted bianthrones and biacridan were studied: 2,2′-bis(trifluoromethyl)bianthrone (**5**), 2,2′-dimethylbianthrone (**6**), and 6,6′-dichloro-2,2′-dimethoxy-*N,N′*-dimethylbiacridan (**7**). The introduction of "tag" substituents (CF_3, CH_3, OCH_3) at positions 2 and 2′ does not effectively change the ground-state steric overcrowding around the "pinch" relative to the parent compound, and yet permits an NMR study of *Z,E* isomerism and isomerization. Tag substituents in the conventional 3 and 3′ positions of bianthrone, proved to be too far removed from the other half of the molecule and unsuited as probes for detection of inequivalent magnetic environment in the two geometrical isomers.

Compound **5** was synthesized as follows.[16] A Grignard reaction of phthalic anhydride and α,α,α-trifluoro-*m*-tolylmagnesium bromide gave *o*-(α,α,α-trifluoro-*m*-toluyl)benzoic acid[17] which was hydrogenated (Pd/C) to *o*-(α,α,α-trifluoro-*m*-tolyl)benzoic acid (mp 111°). HF cyclization of the latter acid afforded 3-trifluoromethyl-10-anthrone (mp 144–145°), which was converted by ferric chloride to the corresponding 9,9′-bianthronyl (mp 235–238°). Enolization (KOH in ethanol) and dehydrogenation ($K_2S_2O_8$) led finally to **5** (mp >300° from xylene, 40% overall yield):[16] uv, λ_{max} (CH_2Cl_2) 234 (log ϵ 4.79), 260 s (4.42), 285 s (4.18), 304 s (4.09), and 398 nm (4.19). Compound **6** (mp >300°)[16] was prepared analogously (22% overall yield): uv, λ_{max} (CH_2Cl_2) 268 (log ϵ 4.50), 290 s (4.29), and 392 (4.21). Compound **7** (mp >300° from bromobenzene)[16] was synthesized by a biomolecular Zn-HCl reduction of 6-chloro-2-methoxy-*N*-methylacridone[18] in ethanol (98% yield): uv, λ_{max} (CH_2Cl_2) 241 (log ϵ 4.71), 302 (4.24), and 446 (4.20). Each compound (**5**, **6**, and **7**) exists in two geometrical forms, *Z* and *E*, as revealed by the NMR spectra: two singlets (in approximately equal population) in the appropriate region, ascribed to the *Z* and *E* isomers (in each geometrical isomer, symmetry causes both substituents to be isochronous). In **5**, the two ^{19}F NMR CF_3 singlets[19] (δ ($CDBr_3$, 298 K) 7.46, 7.72 ppm, $\nu(Z\text{-}\mathbf{5})-\nu(E\text{-}\mathbf{5}) = 21.0 \pm 0.1$ Hz) coalesced at 414 ± 4 K. The process proved to be reversible, characteristic of a dynamic exchange process. The application of the usual coalescence approximation[20,21] leads to the low value of $\Delta G^{\ddagger}_{414K} = 21.3 \pm 0.2$ kcal/mol. Likewise, in **6**, the two ^1H NMR CH_3 singlets (δ($CDBr_3$, 298 K) 2.08, 2.10 ppm, $\nu(Z\text{-}\mathbf{6})-\nu(E\text{-}\mathbf{6}) = 1.9 \pm 0.1$ Hz) coalesced at 357 ± 4 K with $\Delta G^{\ddagger}_{357K} = 20.0 \pm 0.5$ kcal/mol. A similar phenomenon has been revealed in the biacridan derivative (**7**). The ^1H NMR of **7** in 1-bromonaphthalene displayed in the aliphatic region a broad N-CH_3 singlet at 2.57 ppm and two sharp OCH_3 singlets at 3.11 and 3.15 ppm, in the ratio of 1:1. For comparison, the corresponding N-CH_3 signal in *N,N'*-dimethylbiacridan appeared at 2.73 ppm. The two OCH_3 singlets ($\nu(Z\text{-}\mathbf{7})-\nu(E\text{-}\mathbf{7}) = 4.2 \pm 0.1$ Hz at 298 K) coalesced at 373 ± 4 K with $\Delta G^{\ddagger}_{373K} = 20.3 \pm 0.2$ kcal/mol.

The remarkably low barriers associated with the *Z,E* isomerizations of **5**, **6**, and **7**, are interpreted *predominantly* in terms of ground-state destabilization due to steric strain, rather than to a stabilization of diradical transition states. This interpretation is supported by our recent observation on the thermal behavior of 3,3'-dimethyl[$\Delta^{5,5'(12H,12H')}$-binaphthacene]-12,12'-dione (**8**): the linear annelation of **6** (in contrast to **2**[22]) did not lead to faster *Z,E* isomerizations, in spite of the more effective stabilization of a possible diradical transition state.[3] In order to reduce steric interactions, the bianthrone molecule adopts a folded geometry in its ground-state A isomer, and a twisted geometry (about the "pinch") with the two anthrone halves in planar configuration in its B isomer.[4,5] The transition state for the *Z,E* isomerization may be structurally related to B, but with a 90° twist.[23] However, such a transition state should not be located in the free energy diagram too far away from the relatively strained ground-state A isomer. The unusually fast true *Z,E* isomerizations of **5**, **6**, and **7**, are indeed intrinsic properties of the bianthrone and biacridan systems. The low barriers to *Z,E* isomerization reported here are consistent with the contention that the thermochromism, displayed by these systems (in solution or in adsorbed state[13]), is associated with conformational changes.[5]

Acknowledgment. We thank Mr. M. Grinberg of the Weizmann Institute of Science, Rehovot, for the FT ^{19}F NMR determinations.

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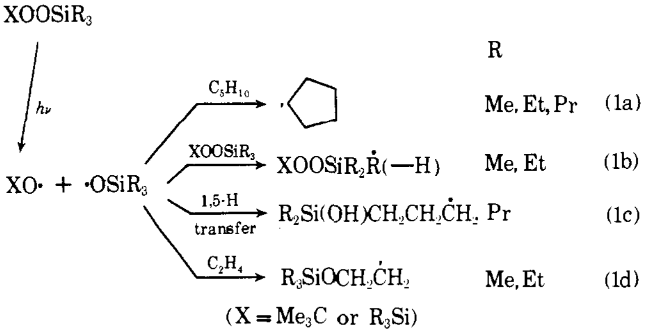
Electron Spin Resonance Studies of the Photolysis of Trialkylsilyl Peroxides

Sir:

The photolysis and thermolysis of dialkyl peroxides (R_3COOCR_3) have been investigated extensively, but little work has been reported on the corresponding metallic peroxides $R_3COOMR'_3$ and R_3MOOMR_3 (M = Si, Ge, Sn, or Pb). We now report a preliminary ESR study of the photolysis of some *tert*-butyl trialkylsilyl peroxides ($Me_3COOSiR_3$) and bis(trialkylsilyl) peroxides ($R_3SiOOSiR_3$).[1,3]

The *tert*-butyl trialkylsilyl peroxides and bis(trialkylsilyl) peroxides show in common the behavior which may be attributed to trialkylsiloxyl radicals (eq 1a–d).



Photolysis of *tert*-butyl trimethylsilyl peroxide and of *tert*-butyltriethylsilyl peroxide ($Me_3COOSiR_3$, R = Me and Et) in cyclopentane showed only the spectrum of the cyclopentyl radical resulting from abstraction of hydrogen by the *tert*-butoxyl and trialkylsiloxyl radicals (reaction 1a); *tert*-butyl tripropylsilyl peroxide under the same conditions showed also the spectrum of the γ-silylpropyl radical $Pr_2Si(OH)CH_2CH_2\dot{C}H_2$ (reaction 1c). In cyclopropane as solvent (which undergoes hydrogen abstraction less readily), the attack occurs mainly on the alkyl group bonded to silicon (reaction 1b); *tert*-butyltrimethylsilyl peroxide