Dynamic Stereochemistry and Steric Effects in Overcrowded Ethylenes. Conformational Behavior of Dixanthylenes

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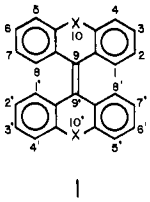
Abstract: The ground-state conformation of 2,2′-disubstituted dixanthylenes (**3**) in solution was investigated by ^1H NMR spectroscopic techniques. The experimental data are consistent with a folded structure. The existence of geometrical isomers in this series is established; the *E*:*Z* ratio in solution depends on the bulkiness of the 2 and 2′ substituents. A DNMR study of **3** revealed low values of free energy of activation for thermal *E*, *Z* isomerization: $\Delta G^{\ddagger}{}_{c} \sim 18$ kcal/mol. These unusual low energy barriers, the lowest yet found in the bistricyclic ethylenes series (**1**), are ascribed predominantly to the high energy contents of the folded ground-state conformations of **3**. In 2,2′-diisopropyldixanthylene (**3c**) a conformational inversion process could be followed in the *E* isomer, apart from the *E*, *Z* isomerization. The $\Delta G^{\ddagger}{}_{c}$ values of both dynamic processes are equal, implying a common transition state which is not the orthogonal biradical $\pi/2$ twisted ethylene. The observed increase in $\Delta G^{\ddagger}{}_{c}$ values with the bulkiness of the 2,2′ substituents is interpreted in terms of [R(2)–H(7′)] type secondary steric interactions in the transition state for the process. Isomerization and topomerization pathways and free-energy profiles, including the postulated folded–twisted transition state, are submitted. The role of the steric interactions in the ground state and in the transition states is discussed.

Introduction

The structural theory stated that there is free rotation about single bonds, while there is no rotation about double bonds. The advent of DNMR[1] spectroscopy has rendered these rules obsolete. Unusually high barriers to rotation involving the tetrahedral carbon atom[2] together with fast isomerizations and topomerizations about formal double bonds[3-6] indicated that there is no exact delineation between carbon–carbon single bonds and double bonds. Thus, the terms, "free rotation" and "hindered rotation" may be associated with both types of linkages.[3]

The potential energy curve for rotation around the olefinic double bond may be regarded as the superposition of two terms: a π electron energy curve (with a maximum at the dihedral angle of $\pi/2$) and a steric strain energy curve (with a maximum at the dihedral angle of 0 in simple ethylenes).[3,7] The positions of the maxima and minima of the resulting potential energy curve representing transition states and ground states for the rotation, respectively, are determined by the relative contributions of both energy terms, at each dihedral angle. The transition state for thermal *E*, *Z* isomerization in simple ethylenes carrying small substituents is the orthogonal (biradical or dipolar) $\pi/2$ twisted ethylene.[3-9] In this case, the potential energy curve for rotation is determined by the π electron energy term. The small steric interactions between the substituents permit a planar ground state. When the steric interactions in the ground state become important, the molecule will deviate from planarity, often by twisting around the double bond.[10,11] Two types of barriers are associated with rotation around the double bond of such "crowded" ethylenes: a steric barrier for passing through the planar form, and a π electronic barrier for the *E*, *Z* isomerization.[11] The absolute and relative magnitudes of these barriers are determined by the electronic stabilization of the $\pi/2$ twisted transition state and by the steric destabilization of the planar structure.[3-9] Steric acceleration of the rate of rotation about polarized carbon–carbon double bond is a well-established phenomenon.[3-7,11-14] Permanently twisted polarized ethylenes in which steric barriers exceed π electronic barriers have recently evoked considerable interest.[11,12]



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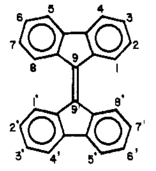
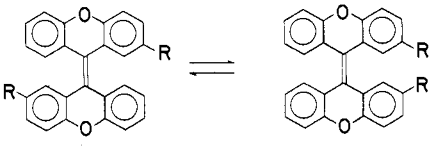


6

2 X=C=O
3 X=O
4 X=CH$_2$
5 X=N-CH$_3$



E-3 Z-3

3a , R=H
3b , R=Me
3c , R=i-Pr
3d , R=t-Bu

The bistricyclic ethylenes (**1**) are attractive substrates for the study of the conformational behavior of symmetrical overcrowded ethylenes.[15-17] An idealized coplanar bistricyclic ethylene would maintain very short nonbonded carbon–carbon and hydrogen–hydrogen distances in the vicinity of the central double bond ("pinch"). The associated repulsive interactions could be relieved by deviations from coplanarity.[15,17] Indeed, an early X-ray crystallographic investigation of the crystal and molecular structure of bianthrone (**2**)[18] indicated that the molecule adopts in the ground state a folded centrosymmetric geometry (the A form): the central rings are boat shaped and the tricyclic halves are folded in opposite directions at the olefinic termini (Figure 1). An X-ray crystallographic investigation of dixanthylene (**3a**) revealed a similar folded structure.[19] On the other hand, the colored forms (B forms) of bianthrone (**2**) and dixanthylene (**3**) were postulated[20] to exist in twisted conformations about the central double bond, with each of the tricyclic halves adopting a planar geometry. In principal, interconversions between folded and twisted forms may occur. In these systems, therefore, the potential energy curve for rotation around the "pinch" would be more complex than in simple ground-state twisted ethylenes.[20]

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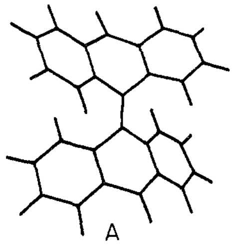

Figure 1. The A form of bianthrone (**2**).

The existence of E, Z isomers and thermal isomerization in the overcrowded bistricyclic system **1** has hardly been noticed.[5,21,22] The "void" of geometrical isomerism served as a basis of a rationale for the thermochromic properties of the bianthrones.[17]

The objective of our investigation was to reveal the dynamic stereochemistry of the symmetrical overcrowded bistricyclic ethylenes (**1**) in solution. Special emphasis was drawn to the role of steric effects in the ground state as well as in the transition states. Representatives of **1** are bianthrone (**2**), dixanthylene (**3**), 10,10,10′,10′-tetrahydrobianthrylidene (**4**), and *N,N′*-dimethylbiacridan (**5**)—all bridged variations of the tetraphenylethylene theme. We have previously reported on the ground-state structure and conformational behavior of the *N,N′*-dimethylbiacridan system.[21-23] The free energy of activation ($\Delta G^{\ddagger}_c$) for E, Z isomerization of 2,2′-disubstituted *N,N′*-dimethylbiacridans (**5**) turned out to be very low: 20-21 kcal/mol. Circumstantial evidence was presented against the traditional $\pi/2$ twisted biradical as the transition state for the thermal E, Z isomerizations.[22,23] Fast E, Z isomerizations were also exhibited in the bianthrone series.[21] The unconventional nature of the proposed isomerization pathway prompted a search for corroborating evidence, both independent and of accumulated weight. Moreover, it was deemed important to determine whether the conformational behavior of *N,N′*-dimethylbiacridans (**5**) and the stereochemical mechanisms derived thereof are a general phenomenon in the bistricyclic ethylenes series. In view of the nonplanarity of the bianthrone (**2**) and *N,N′*-dimethylbiacridan (**5**)[23] systems in solution, a conformational inversion process in appropriately substituted bistricyclic ethylenes (**1**) could be envisioned, in addition to E, Z isomerization.[5] A correlation between the two types of conformational processes might shed light on their pathways. The dixanthylenes (**3**) proved to be favorable substrates for this investigation. The conformation of dixanthylene derivatives has been studied by the dipole-moment method.[24] The thermal stereochemical behavior of few dixanthylene derivatives has been briefly mentioned in a review on kinetics of conformational changes[5] (vide infra).

The related $\Delta^{9(9')}$-bisfluorenylidenes (**6**) should be considered as an exception. In contrast to the folded bianthrone system, the ground state of **6** is apparently twisted.[25-26] Low barriers to E, Z isomerization in **6** were realized by introducing major perturbations in the parent system: steric destabilization of the ground state[27,28,3,5] (by placing bulky substituents at the 1 and 1′ positions), or an enhanced stabilization of a biradical transition state[29] (by benzannelation).

Ground-State Conformation in Solution

The substrates of the present investigation were 2,2′-disubstituted dixanthylenes (**3**). The introduction of tag substituents at the 2 and 2′ positions permits an NMR study of the ground-state conformation, as well as possible Z, E isomerism and thermal isomerization, without altering substantially the steric interactions around the "pinch" (in the ground state) relative to the parent compound. Tag substituents at the 3 and 3′ positions or at the 1 and 1′ positions would be inconvenient and disadvantageous probes for these purposes.[30]

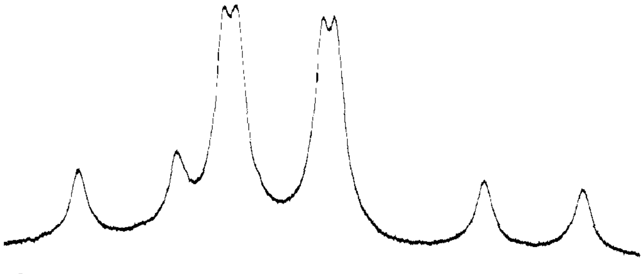

Figure 2. The methyl region of a 250-MHz ^{1}H NMR spectrum of **3c** in $CDCl_3$ (δ, Me_4Si), at 25 °C.

The ^{1}H NMR spectra of all the dixanthylene derivatives (**3**) studied show the presence of the two forms, Z and E (see Experimental Section). Consider the alternative of a *folded* (e.g., A-type) centrosymmetric geometry (in solution). The E isomer has a center of symmetry element (i) while the Z isomer has a C_2 symmetry axis; hence, symmetry causes both substituents in each geometrical isomer to be isochronous. The same conclusion holds true in the case of the alternative *twisted* geometry, in which both the E isomer and the Z isomer have a C_2 symmetry axis. It turned out that the Z:E isomeric ratio depends on the bulkiness of the substituents.[31] It is 1:1.2 in **3b** (R = Me) but differs significantly from 1 in **3c** (R = *i*-Pr) and **3d** (R = *t*-Bu), in accordance with the corresponding steric radii (Table I). This trend is not surprising if a folded geometry is indeed the correct conformation in the ground state. Such a conformation would tend to prevent additional steric interactions between the 2, 2′, 7, and 7′ positions, only as long as the substituents remain small.

In order to verify whether the dixanthylene system adopts a nonplanar (e.g., folded) geometry in solution, the isopropyl prochiral substituent was employed. In a nonplanar molecule, the two methyl groups of the isopropyl prochiral center became diastereotopic and may show chemical shift nonequivalence.[32,33] The methyl region of the 250-MHz ^{1}H NMR spectrum of **3c** is given in Figure 2. It shows the presence of the Z isomer and the E isomer in the ratio of 1:2.3. The "isopropyl" methyl groups of each isomer appear as a double doublet, indicating a lack of a plane of symmetry in the molecule. A decision between the two alternative nonplanar geometries (twisted and folded) could be made on the basis of the ^{1}H NMR absorptions in the aromatic region (Figure 3). The spectrum of the parent compound (**3a**) may be divided into two aromatic regions, one at an exceptionally high field, 6.82-6.91 ppm (4 H), the other at 7.10-7.30 ppm (12 H). In view of the complex pattern of the absorption at the high field, it is ascribed to H(2), H(7), H(2′), and H(7′). The protons ortho to the "pinch" [H(1), H(8), H(1′), and H(8′)] and the protons ortho to the oxygen bridges [H(4), H(5), H(4′), and H(5′)] absorb also at a somewhat high field. In the 2,2′-dialkyldixanthylenes, more than half of the aromatic protons are shielded, while the remaining aromatic protons appear at the normal aromatic region.

The shielding of H(2), H(3), H(2′), and H(7′) and to a lesser degree the shielding of the protons ortho to the "pinch" are due to the effect of the "ring currents" of the opposing benzene rings.[34] The location of positions 2, 7, 2′, and 7′ in the centers of the shielding region is particularly favorable. These results are in accordance with a *folded* structure of dixanthylenes in solution.

By contrast, the shielding of the protons ortho to the "pinch" and of H(2), H(7), H(2′), and H(7′) would be inconsistent with a twisted geometry. Indeed, a downfield shift of these protons is characteristic of the twisted $\Delta^{9(9')}$-bisfluorenylidenes.[34,35]

Table I

A. ^{1}H NMR and Activation Data for the Process $E \rightarrow Z$ (Major → Minor Conformer)

compd	R in **3**	solvent	$\Delta\nu T_c$, Hz	T_c, K	$\Delta G^{\ddagger}_c$, kcal/mol	$\Delta G^{\ddagger}_i$, kcal/mol	ΔG°, kcal/mol
3b	Me	$CDBr_3$	2.6 ± 0.1[a]	317 ± 3	17.5 ± 0.3	17.1 ± 0.3	0.10 ± 0.05
3c	*i*-Pr[b]	$CDCl_3$	3.40 ± 0.05[c]	320 ± 3	17.9 ± 0.3	17.5 ± 0.3	0.37 ± 0.07
3d	*t*-Bu	1-bromonaphthalene	3.9 ± 0.1[a]	319 ± 3	18.4 ± 0.3	18.0 ± 0.3	1.10 ± 0.08

B. ^{1}H NMR and Activation Data for the Conformational Inversion Process of *E*-**3c**[d]

$\Delta\nu$ (Hz, at 250 MHz)	T_c (K)	$\Delta G^{\ddagger}_c$ (kcal/mol)	$\Delta G^{\ddagger}_i$ (kcal/mol)
0.90 ± 0.05	309 ± 3	17.7 ± 0.5	17.3 ± 0.5

[a] At 100 MHz. [b] The data refer to the methine heptets. [c] At 250 MHz. [d] The data refer to the equally populated two doublets of the "isopropyl" methyl groups.

Dynamic Behavior

The thermal conformational behavior of **3** in solution was investigated by the DNMR[1,5,36] method. 2,2′-Diisopropyldixanthylene (**3c**), with its prochiral substituents, contributed a new dimension to the present study. In **3c**, two conformational thermal processes could be monitored independently in the ^{1}H NMR spectra: (1) *E, Z* isomerization; (2) conformational inversion process in the *E* isomer. Process (1) was revealed by the coalescence of the two heptets representing the methine protons of the isopropyl groups ($CH(CH_3)_2$) in the two isomers. Process (2) could be followed by the coalescence (to a single doublet) of the two doublets representing the diastereotopic "isopropyl" methyl groups ($CH(CH_3)_2$) in the *E* isomer, i.e., the more heavily populated form. These anisochronous methyl groups become enantiotopic and equivalent in the rapidly inverting molecule (on the NMR time scale). The difference in their chemical shifts is very small while the corresponding signals in the *Z* isomer are considerably shifted from each other and from the signals of the *E* isomer. The coalescence of the methyl doublets of the *E* isomer could be achieved at a sufficiently low temperature that would leave the sharp methyl doublets of the *Z* isomer intact. Under these conditions, the signals of the *Z* isomer are still unaffected by the kinetic broadening due to either the *E, Z* isomerization or the conformational inversion in the *Z* isomer.

Table I summarizes the ^{1}H DNMR results. The data were calculated by the usual coalescence approximation[1,5,36] or the graphic method approximation,[37] applying Eyring's formula. It is now generally accepted[38,39] that these methods give good approximations of the free energy of activation at the coalescence temperature, $\Delta G^{\ddagger}_c$. Usually, $\Delta G^{\ddagger}_c$ values are the only reliable parameters obtained from the DNMR method, whereas substantial errors may be involved in the corresponding enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) parameters obtained by this method.[1,5,36,38-42] $\Delta\nu$ values were not changed with temperature near the coalescence region. The data of $\Delta G^{\ddagger}_c$ in Table I are the "formal" free energy of activation values for the process $E \rightarrow Z$ or for the conformational inversion in *E*-**3c.** They were calculated from the rate constants at the coalescence temperature, assuming a value of unity for the transmission coefficient in Eyring's formula (vide infra). The $\Delta S^{\ddagger}$ values for monomolecular conformational isomerizations such as described above are expected to be similar and essentially close to zero.[3,5,8,36,42,43] Thus, valid conclusions may be drawn by comparing $\Delta G^{\ddagger}_c$ values, provided that the temperature range applied in their evaluation remains narrow (as indeed is the case in the present study).

The conformational changes studied by the DNMR method may be considered a series of consecutive monomolecular reactions, in which all intermediates, reactants, and products are in a true equilibrium.[42,44-46] The only species detected by the method are the starting and final structures that interconvert. One usually assumes that the overall first-order rate constant obtained by the method is determined by the rate of passage through the rate-determining activation state, i.e., the transition state at the top of the highest barrier.[45,47]

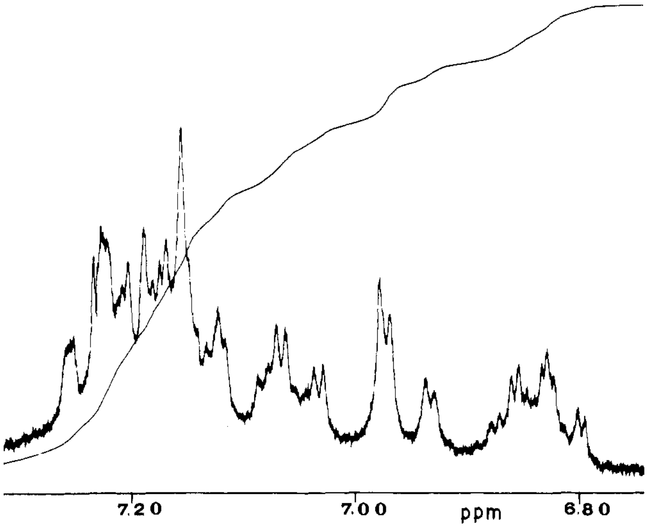

Figure 3. The aromatic region of a 250-MHz ^{1}H NMR spectrum of **3c** in $CDCl_3$ (δ, Me_4Si) at 25 °C.

The fundamental result indicated in Table I is the low values of $\Delta G^{\ddagger}_c$ for the thermal *E, Z* isomerizations of the 2,2′-disubstituted dixanthylenes: $\Delta G^{\ddagger}_c \approx 18$ kcal/mol. These exceptionally low rotational energy barriers for an ethylenic system are attributed *predominantly* to the high energy contents of the folded ground-state conformations. In an idealized planar model of the dixanthylene, the substantial overlaps of the van der Waals radii at the 1, 1′, 8, and 8′ position result in strong primary steric interactions. In order to relieve these repulsive interactions,[15,31,48-50] the molecule deviates from coplanarity and adopts the folded geometry in the ground state. The fast rates of *E, Z* isomerization of **3b–d** indicate that the folded conformations are of relatively high energy owing to the transmission of primary steric interactions into π and σ electronic strain. *Ground-state destabilization* is thus the main contributor to the fast thermal *E, Z* isomerizations of these systems.

The most remarkable finding depicted in Table I is the equality of the $\Delta G^{\ddagger}_c$ values of the *E, Z* isomerization and the conformational inversion in the *E* isomer of 2,2′-diisopropyldixanthylene. This conclusion is supported by the following results of ^{1}H NMR decoupling experiments performed at the methyl region of the isopropyl groups of **3c.** Irradiation at the high-field doublet (δ 0.964 ppm, $J = 6.9$ Hz) associated with the *Z* isomer, at 40 °C, affected concomitantly both the second doublet (δ 1.080 ppm, $J = 6.9$ Hz) associated with the *Z* iso-

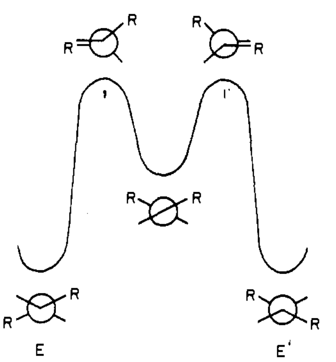

Figure 4. Proposed free-energy profile and topomerization pathway of conformational inversion in E-**3c**.

mer (conformational inversion) and the two doublets (δ 1.036, 1.040 ppm, $J = 6.9$ Hz) associated with the E isomer ($Z \rightarrow E$ isomerization). No spectral changes were observed when the decoupling experiment was performed at 21 °C; at this temperature, both conformational processes were slowed down. Hence, the rate constant of the conformational inversion is of the same order of magnitude as that of the E,Z isomerization. This equality in the $\Delta G^{\neq}{}_c$ values of the two conformational processes is not fortuitous. It argues in favor of a *common highest transition state* (HTS) in their free-energy profiles.

The conformational inversion process in E-**3c** (as revealed by the collapse of its diastereotopic methyl groups which become enantiotopic in the limit of fast inversion) has to pass through a genuine planar transition state or some time-averaged planar structure thereof. The $\pi/2$ twisted (biradical) ethylene does not have a plane of symmetry passing between the methyl groups of the isopropyl substituents. Consequently, the conformational inversion does not have to pass through this $\pi/2$ twisted form, either as the transition state or elsewhere along the reaction pathway. Furthermore, a fully planar transition state would not be acceptable because it would involve two high-energy H(1)-H(8′) type repulsive steric interactions. It is reasonable to assume that these unfavorable interactions are encountered successively, one at a time, during the conformational inversion process.[51] This pathway still implies a time-average planar structure, as required. The proposed scheme for the conformational inversion of E-**3c** and its free-energy profile are given in Figure 4. This single minimum potential involves two mirror-imaged transition states and a nonorthogonal twisted ethylene as an intermediate. In each of these folded-twisted transition states (F-T TS), only one primary H(1)-H(8′) type and one secondary R(2)-H(7′) type steric interactions are realized.

As noted previously, the conformational inversion pathway never passes through the orthogonal $\pi/2$ twisted ethylene. Therefore, the requirement of a common HTS for both conformational processes rules out the traditional orthogonal transition state for the E, Z isomerization. The F-T TS for the conformational inversion should serve also as the HTS of the E, Z isomerization. The proposed scheme for the E, Z isomerization and its free-energy profile are given in Figure 5. This scheme implies a double minimum potential. It takes into account only one-way rotations that prevent the somewhat higher energy R(2)-R(2′) type steric interactions. It is obvious that the pattern of the E, Z isomerization scheme is more complex than that encountered in E, Z isomerizations of ground-state twisted ethylenes. The traditional $\pi/2$ twisted ethylene appears along the isomerization pathway only as a transition state between two partially twisted ethylene intermediates, but not as the HTS. The third transition state originates from the Z isomer. Its structure is also folded-twisted. However, it is somewhat lower in energy than the former, involving only one H(1)-H(8′) type steric interaction and avoiding any R(2)-H(7′) type ones.

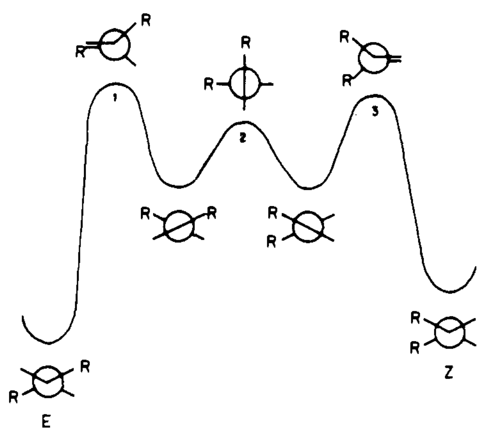

Figure 5. Proposed free-energy profile and isomerization pathway of E, Z isomerization in **3**.

The experimental evidence leads to the conclusion that in these overcrowded systems, the pure π-electronic barrier is lower in energy than the barrier associated with the HTS. The latter barrier is determined by combination of steric (H(1)-H(8′) and R(2)-H(7′) type) interactions, and partial loss of π electronic overlap by twisting about the "pinch". The possibility of stabilizing the biradical $\pi/2$ twisted structure by delocalization in the four phenyl substituents renders its energy lower than the energy of the proposed HTS.[52] The conformational behavior of these systems is thus determined mainly by the steric interactions around the "pinch".[53] The proposed HTS of the E, Z isomerization in the dixanthylene series is consistent with the calculated dependence of the strain energy on torsion around the "pinch" in the closely related bianthrone system.[20]

In calculating the $\Delta G^{\neq}{}_c$ values of both conformational processes, the value of the transmission coefficient κ in Eyring's formula has been taken as 1. As recalled, the energy profile of the conformational inversion is symmetrical, with two mirror-imaged transition states of equal energy. The molecule of the E isomer, after passing the first transition state, may continue and complete the conformational inversion by passing the second transition state. However, it may also revert through the original first transition state. The probability of these two possible pathways is equal. Thus, the rate of passage through the first barrier of the inversion process is twice the rate of the inversion followed by the DNMR method. The free energy of activation of the first step, $\Delta G^{\neq}{}_1$, may be calculated from the overall rate constant and Eyring's formula, assuming a value of $^1/_2$ for the transmission coefficient. The same value may be taken in the calculation of $\Delta G^{\neq}{}_1$ of the E, Z isomerization process, assuming that the energies of the first transition state and the third transition state are close. The same procedure has been applied in calculating the first free-energy barrier for inversion in cyclohexane, for which a similar energy profile has been postulated.[54] Each of the $\Delta G^{\neq}{}_1$ values given in Table I is lower than the corresponding $\Delta G^{\neq}{}_c$ value by 0.4 kcal/mol, as the coalescence temperatures in all cases fall within a very narrow range. The fundamental conclusions drawn from the $\Delta G^{\neq}{}_c$ values hold true when $\Delta G^{\neq}{}_1$ values and their comparison are considered.

The introduction of alkyl substituents at the 2 and 2′ positions of the dixanthylene system permits an evaluation of the dependence of $\Delta G^{\neq}{}_c$ (or $\Delta G^{\neq}{}_1$) for the $E \rightarrow Z$ isomerization on the "size" of the substituent. The role of the "size" ("spatial requirement") of the substituents in evaluating conformational processes has recently been emphasized.[31] The picture that emerges in the case of **3** is a notable increase in the free energy

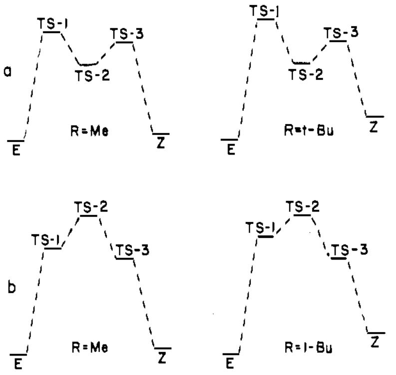

Figure 6. Comparison of the two extreme free-energy profiles of *E*, *Z* isomerization in **3b** and **3d**: (a) TS-1 is HTS; (b) TS-2 is HTS.

of activation of the $E \rightarrow Z$ isomerization on going to a bulkier substituent. This trend is contrary to the traditional decrease in $\Delta G^{\ddagger}{}_{c}$ values in substituted ground-state twisted ethylenes upon increasing the "size" of the substituent.[3-7,11-14] The observed increase in $\Delta G^{\ddagger}$ ($\Delta G^{\ddagger}{}_{c}$ or $\Delta G^{\ddagger}{}_{1}$) with the bulkiness of the substituents at positions 2 and 2′ supports the proposed HTS of the *E*, *Z* isomerization (Figure 5). In the ground state, the folded structure tends to prevent additional steric interactions between the 2, 2′, 7, and 7′ positions. In the F-T TS, the secondary R(2)-H(7′) type steric interactions become more important, and could thus account for the observed trend in the $\Delta G^{\ddagger}$ values. This trend would be inconsistent with the formation, at the rate-determining step, of an orthogonal biradical transition state, in which both primary H(1)-H(8′) type and secondary R(2)-H(7′) type interactions are avoided. Although the overall steric effect on $\Delta G^{\ddagger}$ in the $E \rightarrow Z$ process ($\Delta G^{\ddagger}$ (**3d**, R = *t*-Bu) − $\Delta G^{\ddagger}$ (**3b**, R = Me)) is only 0.9 kcal/mol, it is well beyond the experimental error involved in evaluating $\Delta G^{\ddagger}$ values by the DNMR method. This effect, first observed in the *N*,*N*′-dimethylbiacridan series (**5**),[22,23] is maintained in the dixanthylenes. It should be noted that the observed trend in $\Delta G^{\ddagger}$ appears only in the $E \rightarrow Z$ isomerization, while $\Delta G^{\ddagger}$ of the reverse $Z \rightarrow E$ isomerization remains constant throughout the series. This difference in substituent dependency is reflected in the shape of the double minimum energy profile of the *E*, *Z* isomerizations. Consider the effects of the methyl → *tert*-butyl transformation on the ground states of *E*-**3** and *Z*-**3** and on the transition states involved in the *E*, *Z* isomerizations. It is reasonable to assume that the ground-state energy of *E*-**3b** would hardly be altered by the transformation, while the ground state of *Z*-**3b** would be destabilized due to the more effective unfavorable repulsive interaction between the bulkier substituents. This is indeed reflected in the variation of the relative *E* and *Z* populations. A priori, two double minimum free energy profiles may be visualized, each involving three consecutive transition states, TS-1, TS-2, and TS-3 (having the same structures as depicted in Figure 5): profiles a and b (Figure 6). Only TS-1, which involves R(2)-H(7′) type steric interactions, may be influenced by an increase in the size of the substituents at positions 2 and 2′. TS-2 and TS-3 are expected to be insensitive to the size of the 2 and 2′ substituents: in these transition states interactions with the 2 and 2′ positions are avoided. The HTS in profile a and profile b are TS-1 and TS-2, respectively. In profile a, an increase in $\Delta G^{\ddagger}$ ($E \rightarrow Z$) on going to the bulkier substituent is expected, whereas $\Delta G^{\ddagger}$ ($Z \rightarrow E$) is predicted to be constant or to increase or decrease slightly (depending on whether the destabilizing steric interactions are more pronounced in the ground state or in the transition state). In profile b, $\Delta G^{\ddagger}$ ($E \rightarrow Z$) is expected to be constant or decrease slightly, whereas $\Delta G^{\ddagger}$ ($Z \rightarrow E$) should decrease in the series, thus relieving the destabilizing steric interactions in the ground state of *Z*. The experimental evidence is inconsistent with profile b, thus strengthening the arguments in favor of profile a.[53]

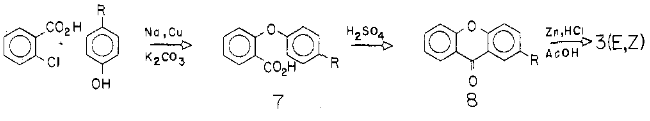

Figure 7. Synthesis of dixanthylenes (**3**).

It is not clear to what extent the experimental increase in the $\Delta G^{\ddagger}$ values with the steric radius of the 2 and 2′ substituents represents an increase in $\Delta H^{\ddagger}$ (due to an enhanced steric strain in the TS) or a decrease in $\Delta S^{\ddagger}$ (due to an enhanced steric hindrance of motions in the TS).[15,31,50,55] Both terms contribute to $\Delta G^{\ddagger}$ in the same direction, consistently with the proposed structure of the HTS.

Finally, the possible role of the oxygen "bridges" in the conformational behavior of the dixanthylene system should be considered. The free-energy barriers to thermal *E*, *Z* isomerizations in **3** were the lowest obtained among the bistricyclic ethylenes (**1**): $\Delta G^{\ddagger}{}_{c}$ = 17.5–18.4 kcal/mol.[21-23] The analysis of the effect of the bridges on the dynamic stereochemistry of **1** is reserved until comprehensive information on the **1** series becomes available.

Synthetic Approach

The synthesis of the model 2,2′-disubstituted dixanthylenes (**3**) is outlined in Figure 7. The synthetic scheme was based on known reactions; however, the application to new derivatives required several modifications of the known methods (see Experimental Section). The substituted *o*-phenoxybenzoic acids (**7**) were obtained by Ullmann condensations of the appropriately para-substituted phenols with *o*-chlorobenzoic acid, a modification of the method of Dahr.[56] Cyclization of **7** with H_2SO_4 yielded the 2-substituted xanthones (**8**). These were converted to 2,2′-disubstituted dixanthylenes (**3**) by a bimolecular Zn-HCl reduction in glacial acetic acid, following the classical method for the preparation of dixanthylene.[24,57]

Experimental Section

General. The ^1H DNMR spectra were obtained using Varian HA-100, Bruker WH-270, or Cameca 250-MHz spectrometers equipped with a variable-temperature unit. The NMR changes proved to be reversible and characteristic of a dynamic exchange. Temperatures were measured with ethylene glycol using the substitution technique and the Varian or Cameca correlation charts, and are considered accurate within ±2 °C. ^1H NMR spectra were obtained using internal locking and the data (usually at 100 MHz, otherwise frequency indicated) are reported in parts per million downfield from Me_4Si as internal reference (δ units). IR spectra were recorded on a Perkin-Elmer 457 spectrometer. Electronic spectra were recorded on a Unicam SP-800 spectrometer. Mass spectra were recorded on a Varian MAT 311 spectrometer. Melting points were measured on a Fisher-Jones capillary melting point apparatus and are uncorrected. Samples were dried over P_2O_5 under vacuum (ca. 1 mm), usually at 100 °C, before analysis. No attempts were made to optimize yields.

***o*-(*p*-Isopropylphenoxy)benzoic Acid (7c).** *p*-Isopropylphenol (23.7 g, 0.17 mol), *o*-chlorobenzoic acid (25.2 g, 0.16 mol), anhydrous K_2CO_3 (5.5 g, 0.04 mol), and 0.3 g of copper-bronze were added to a solution of sodium methoxide (from 3.8 g (0.16 mol) of sodium) in methanol (80 mL). The methanol was distilled off within ~90 min at 110–120 °C (oil bath), and the temperature was raised within ~30 min to 200 °C and kept at this temperature for ~0.75 h. The reaction mixture solidified at about 150 °C, melted at higher temperature, and finally solidified again at 200 °C. The reaction mixture was treated while still hot with water (ca. 20 mL) and, after cooling, dichloromethane was added and the product was extracted with aqueous Na_2CO_3 solution. The aqueous layer was filtered and acidified (HCl) and the precipitating acid was filtered off and washed with hot water to remove unreacted *o*-chlorobenzoic acid. Recrystallization from toluene-petroleum ether (bp 40–60 °C), 1:9, gave the acid (**7c**) as colorless crystals: mp 109–110 °C; yield 35%; IR (Nujol) 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.25 (d, J = 7 Hz, 6 H), 2.83 (h, J = 7 Hz, 1 H), 6.75–7.55 (m, 7 H), 8.17 (dd, J_1 = 7, J_2 = 2 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ) 227 (4.04), 288 (3.48); *m/e* 256 (M^+, 44%), 121 (100%). Anal. ($C_{16}H_{16}O_3$) C, H.

***o*-(*p*-Toluoxy)benzoic acid (7b)** was prepared from *p*-cresol by the procedure described above for **7c**, in 44% yield. It was obtained as colorless crystals: mp 120–122 °C (from benzene-petroleum ether (bp 40–60 °C), 1:1) (lit.[58] mp 118.5 °C); IR (Nujol) 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 6.80–7.54 (m, 7 H), 8.15 (dd, J_1 = 2, J_2 = 8 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ), 231 (4.06), 287 (3.57); *m/e* 228 (M^+, 45%), 122 (100%). Anal. ($C_{14}H_{12}O_3$)C, H.

***o*-(*p*-*tert*-Butylphenoxy)benzoic acid (7d)** was prepared from *p*-*tert*-butylphenol[59] by the procedure described above for **7c**, in 39% yield. It was obtained as colorless crystals: mp 127–130 °C (from benzene-petroleum ether (bp 40–60 °C)); IR (Nujol) 1650 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 6.80–7.50 (m, 7 H), 8.16 (dd, J_1 = 2, J_2 = 7 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ), 226 (3.96), 285 (3.34); *m/e* 270 (M^+, 30%), 255 ($[M - CH_3]^+$, 100%). Anal. ($C_{17}H_{18}O_3$) C, H.

2-Isopropylxanthone (8c). The acid **7c** (10 g) was added to concentrated H_2SO_4 (100 mL) and the mixture was heated with magnetic stirring for ~30 min at 100 °C.[56,60] The reaction was terminated by pouring the mixture on cold water. The gray precipitate was collected and washed with 5% aqueous sodium bicarbonate and water. The crude product was dissolved in chloroform and undissolvable materials were removed by filtering. The filtrate was evaporated and the residue was recrystallized from ethyl acetate. **8c** was obtained in 92% yield as colorless crystals: mp 82–84 °C; IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.30 (d, J = 7 Hz, 6 H), 3.00 (h, J = 7 Hz, 1 H), 7.20–7.80 (m, 5 H), 8.16 (d, J = 2 Hz, 1 H), 8.32 (dd, J_1 = 2, J_2 = 7 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ), 242 (4.62), 262 (4.10), 288 (3.62), 292 (3.62), 342 (3.81); *m/e* 238 (M^+, 93%), 223 ($[M - CH_3]^+$, 100%). Anal. ($C_{16}H_{14}O_2$) C, H.

2-Methylxanthone (8b) was prepared from **7b** by the procedure described above for **8c** in 90% yield. It was obtained as colorless crystals: mp 120–121 °C (lit.[58] mp 121 °C) (from ethyl acetate); IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 7.20–7.80 (m, 5 H), 8.10 (s, 1 H), 8.31 (dd, J_1 = 2, J_2 = 8 Hz, 1 H); UV λ_{max} (EtOH), nm (log ϵ), 244 (4.21), 262 (4.10), 288 (3.64), 293 (3.64), 344 (3.86); *m/e* 210 (M^+, 100%). Anal. ($C_{14}H_{10}O_2$) C, H.

2-*tert*-Butylxanthone (8d) was prepared from **7d** by the procedure described above for **8c** in 96% yield. It was obtained as colorless crystals: mp 106–108 °C (from ethyl acetate); IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H), 7.20–7.80 (m, 5 H), 8.20–8.40 (m, 2 H); UV λ_{max} (EtOH), nm (log ϵ), 242 (4.60), 262 (4.02), 282 (3.54), 292 (3.54), 341 (3.73); *m/e* 252 (M^+, 16%), 237 ($[M - CH_3]^+$, 100%). Anal. ($C_{17}H_{16}O_2$) C, H.

2,2′-Diisopropyldixanthylene (3c). To a boiling, magnetically stirred solution (135–140 °C, oil bath) of **8b** (2 g) in glacial AcOH (20 mL), zinc powder (1.2 g) was added, and the mixture was refluxed for 1 h. A few drops of concentrated HCl were introduced from time to time (total amount, 2 mL). The reaction mixture was cooled, methanol (10 mL) was added, and the precipitating product was filtered off. **3b** was obtained as a bluish powder, mp 212–213 °C (with intensive blue-green coloration) (from ethyl acetate) in 75% yield: IR (Nujol) 1604, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.96–1.04 (m, 12 H), 2.56–2.76 (m, 2 H), 6.79–7.29 (m, 14 H); isopropyl absorptions δ *E* (Me) 1.036, 1.040 (2 d, J = 6.9 Hz, 70%), δ *E* (CH) 2.664 (h, J = 6.9 Hz, 64%), δ *Z* (Me) 0.964, 1.080 (2 d, J = 6.9 Hz, 30%), δ *Z* (CH) 2.649 (h, J = 6.9 Hz, 36%), $\nu_{E_1} - \nu_{E_2}$ (Me signals) 0.90 Hz, $\nu_E - \nu_Z$ (CH signals) 3.8 Hz; UV λ_{max} (CH_2Cl_2), nm (log ϵ), 235 (4.25), 256 (4.15), 283 (4.03), 368 (4.24); *m/e* 444 (M^+, 100%). Anal. ($C_{32}H_{28}O_2$) C, H.

2,2′-Dimethyldixanthylene (3b) was prepared from **8b** by the procedure described above for **3c** in 70% yield. It was obtained as a bluish powder: mp 264–265 °C (with strong blue-green coloring) (lit.[60] mp 262 °C) (from toluene-petroleum ether (bp 40–60 °C, 1:1)); IR (Nujol) 1604, 1593 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.05, 2.08 (2 s, 1.18:1, 6 H), 6.70–7.20 (m, 14 H), $\nu_E - \nu_Z$ (Me signals) 2.6 Hz; UV λ_{max} (CH_2Cl_2), nm (log ϵ), 238 (4.13), 258 (4.09), 284 (4.01), 370 (4.23); *m/e* 388 (M^+, 100%). Anal. ($C_{28}H_{20}O_2$) C, H.

2,2′-Di-*tert*-butyldixanthylene (3d) was prepared from **8d** by the procedure described above for **3c** in 64% yield. It was obtained as a bluish powder: mp 260–262 °C, change of solid state through liquid, 292–294 °C melts (with strong blue-green coloring) (from xylene); IR (Nujol) 1604, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.069, 1.094 (2 s, 1:5.6, 18 H), 6.81–7.27 (m, 14), (1-bromonaphthalene, 100 MHz) 0.91, 0.95 (2 s, 1:5.6), $\nu_E - \nu_Z$ (*t*-Bu signals) 3.9 Hz; UV λ_{max} (CH_2Cl_2), nm (log ϵ), 237 (4.14), 258 (4.03), 283 (3.93), 370 (4.16); *m/e* 472 (M^+, 100%). Anal. ($C_{34}H_{32}O_2$) C, H.

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References and Notes

(1) Jackman, L. M.; Cotton, F. A., Ed. "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press: New York, N.Y., 1975.
(2) Oki, M. *Angew. Chem., Int. Ed. Engl.* **1976,** *15,* 87.
(3) Kalinowski, H. O.; Kessler, H. *Top. Stereochem.* **1973,** *7,* 295.
(4) Jackman, L. M. in ref 1, p 203.
(5) Sutherland, I. O. *Annu. Rep. NMR Spectrosc.* **1971,** *4,* 71.
(6) Kessler, H. *Tetrahedron* **1974,** *30,* 1861.
(7) Sandström, J.; Wennerbeck, I. *J. Chem. Soc., Chem. Commun.* **1971,** 1088.
(8) Cundall, R. B. *Prog. React. Kinet.* **1964,** *2,* 165.
(9) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972,** *11,* 92.
(10) Ammon, H. L.; Wheeler, G. L. *J. Am. Chem. Soc.* **1975,** *97,* 2326.
(11) Sandström, J.; Sjöstrand, U. *Tetrahedron* **1978,** *34,* 371.
(12) Sandström, J.; Sjöstrand, U.; Wennerbeck, I. *J. Am. Chem. Soc.* **1977,** *99,* 4526.
(13) Shvo, Y. *Tetrahedron Lett.* **1968,** 5923.
(14) Downing, A. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. B* **1969,** 111.
(15) The available data on the conformational behavior of symmetrical overcrowded ethylenes is scarce. Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976,** *76,* 311.
(16) There is recent renewed activity in the field of overcrowded ethylenes: Olah, G. A.; Surya Prakash, G. K. *J. Org. Chem.* **1977,** *42,* 580. Feringa, B.; Wynberg, H. *J. Am. Chem. Soc.* **1977,** *99,* 602.
(17) Reviews on the structure and the thermochromic, photochromic, and piezochromic properties in this series: Kortüm, G. *Ber. Bunsenges. Phys. Chem.* 1974, *78,* 391. Bercovici, T; Korenstein, R; Muszkat, K. A.; Fischer, E. *Pure Appl. Chem.* **1970,** *24,* 531. Day, J. H. *Chem. Rev.* **1963,** *63,* 65. Bergmann, E. D. *Prog. Org. Chem.* **1955,** *3,* 81.
(18) Harnic, E.; Schmidt, G. M. J. *J. Chem. Soc.* **1954,** 3295. Harnic, E.; Herbstein, F. H.; Schmidt, G. M. J.; Hirshfeld, F. L. *ibid.* **1954,** 3288.
(19) Mills, J. F. D.; Nyburg, S. C. *J. Chem. Soc.* **1963,** 308, 927.
(20) (a) Korenstein, R.; Muszkat, K. A.; Sharafy-Ozeri, S. *J. Am. Chem. Soc.* **1973,** *95,* 6177. (b) Korenstein, R.; Muszkat, K. A.; Slifkin, M. A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1976,** 438.
(21) Agranat, I.; Tapuhi, Y. *J. Am. Chem. Soc.* **1976,** *98,* 615.
(22) Agranat, I.; Tapuhi, Y. *Nouveau J. Chim.* **1977,** *1,* 361.
(23) Agranat, I.; Tapuhi, Y. *J. Am. Chem. Soc.*, **1978,** *100,* 5604.
(24) Bergmann, E. D.; Weiler-Feilchenfeld, H.; Heller, A.; Britzmann, C.; Hirschfeld, A. *Tetrahedron, Suppl. 7* **1966,** 349.
(25) Bailey, N. A.; Hull, S. E. *Chem. Commun.* **1971,** 960.
(26) Bailey, N. A.; Hull, S. E. *Acta Crystallogr., Sect. B* **1978,** *34,* 3289.
(27) Gault, I. R.; Ollis, W. D.; Sutherland, I. O. *Chem. Commun.* **1970,** 269.
(28) Agranat, I.; Rabinovitz, M.; Weitzen-Dagan, A.; Gosnay, I. *J. Chem. Soc., Chem. Commun.* **1972,** 732.
(29) Rabinovitz. M.; Agranat, I.; Weitzen-Dagan, A. *Tetrahedron Lett.* **1974,** 1241.
(30) In the bianthrone series, tag substituents at the 3 and 3′ positions proved to be too far away from the other half of the molecule and therefore unsuitable probes for detection of inequivalent magnetic environment in the two geometrical isomers by conventional NMR techniques. On the other hand, the introduction of substituents at the 1 and 1′ positions leads (in most cases) to the exclusive formation of *E* isomers because of enhanced steric repulsions in the corresponding *Z* isomers.
(31) Förster, H.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1977,** *16,* 429.
(32) Mislow, K.; Raban, M. *Top. Stereochem.* **1967,** *1,* 1.
(33) Jennings, W. B. *Chem. Rev.* **1975,** *75,* 307.
(34) Bartle, K. D.; Jones, D. W. *Adv. Org. Chem.* **1972,** *8,* 317.
(35) Rabinovitz, M.; Agranat, I.; Bergmann, E. D. *Tetrahedron Lett.* **1965,** 1265.
(36) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970,** *9,* 219.
(37) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970,** *74,* 961. A convenient numerical solution is available from Mislow, K. (Dissertation by Egan, W.), Princeton University.
(38) Kost, D.; Carlson, E. H.; Raban, M. *Chem. Commun.* **1971,** 656.
(39) Kost, D.; Zeichner, A. *Tetrahedron Lett.* **1974,** 4533. Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1971,** *93,* 6205. Bernard, M.; Canuel, L.; St-Jacques, M. *ibid.* **1974,** *96,* 2929. Newman, R. C.; Jonas, V. *J. Org. Chem.* **1974,** *39,* 925. Dahlquist, K. I.; Forsen, S.; Alm, T. *Acta Chem. Scand.* **1970,** *24,* 651. Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975,** *97,* 3660.
(40) Allerhand, A.; Gutowsky, H. S.; Jonas, J.; Meinzer, R. A. *J. Am. Chem. Soc.*

1966, *88,* 3185.
(41) Shoup, R. R.; Becker, E. D., McNeel, M. L. *J. Phys. Chem.* **1972,** *76,* 71.
(42) Anet, F. A. L.; Anet, R. "Determination of Organic Structures by Physical Methods", Vol. 3; Nachod, F. C.; Zuckerman, J. J., Ed.; Academic Press: New York, N.Y., 1971; Chapter **7,** p 344. Anet, F. A. L.; Anet, R. In ref 1, Chapter 14, p 543.
(43) Lehn, J. M. *Fortschr. Chem. Forsch.* **1970,** *15,* 311.
(44) Glasstone, S.; Laidler, K.J., Eyring, H. "The Theory of Rate Processes," International Chemical Series, McGraw-Hill: New York, N.Y., 1941.
(45) Reference 44, pp 99–100 and 199–200.
(46) (a) Binsch, G. In ref 1, Chapter 15, p 621. (b) Grunwald, E.; Ralph, E. K. In ref 1, Chapter 3, p 45.
(47) Raban, M.; Kenney, G. W. J., Jr. *Tetrahedron Lett.* **1969,** 1295.
(48) Mislow, K. "Introduction to Stereochemistry", W. A. Benjamin: New York, N.Y., 1965; p 38.
(49) Newman, M. S., Ed. "Steric Effects in Organic Chemistry", Wiley: New York, N.Y., 1956.
(50) (a) Westheimer, F. H. In ref 49, p 523. (b) Taft, R. W., Jr. In Ref 49, p 556.
(51) For a similar approach in the elucidation of isomerization pathways in other systems see, e.g., Kost, D.; Sprecher, M. S. *Tetrahedron Lett.* **1977,** 1089. Kost, D.; Raban, M. *J. Org. Chem.* **1976,** *41,* 1748. Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1975,** *97,* 2209.
(52) The activation energy of *E, Z* isomerization in 1,2-dideuterioethylene is 65.0 kcal/mol (Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955,** *23,* 315), whereas in 1,2-diphenylethylene it is 42.8 kcal/mol (Kistiakowsky, G. B.; Smith, W. R. *J. Am. Chem. Soc.* **1934,** *56,* 638).
(53) Cf. ref 5 for a different view on the isomerization pathway in a related few bianthrone and dixanthylene derivatives.
(54) Jensen, F. R.; Noyce, D. S.; Sederholm, Ch.H.; Berlin, A. J. *J. Am. Chem. Soc.* **1962,** *84,* 386. Anet, F. A. L.; Bourn, A. J. R. *ibid.* **1967,** *89,* 760. Bovey, F. A.; Anderson, E. W.; Hood, F. P.; Kornegay, R. L. *J. Chem. Phys.* **1964,** *40,* 3099. Pickett, H. M.; Strauss, H. L. *J. Am. Chem. Soc.* **1970,** *92,* 7281. Harris, R. K.; Spragg, R. A. *J. Chem. Soc. B* **1968,** 684.
(55) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1953,** *75,* 4534.
(56) Dhar, S. N. *J. Chem. Soc.* **1920,** 1053.
(57) Gurgenjanz, G.; v. Kostanecki, S. *Ber.* **1895,** *28,* 2310.
(58) Ullmann, F.; Zlokasoff, M. *Ber.* **1905,** *38,* 2111.
(59) Huston, R. C.; Hsieh, T. Y. *J. Am. Chem. Soc.* **1936,** *58,* 439.
(60) Mustafa, A.; Asker, W.; Sobhy, M. E.-D. *J. Org. Chem.* **1960,** *25,* 1519.

Heats of Hydrogenation and Formation of Linear Alkynes and a Molecular Mechanics Interpretation[1]

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Abstract: The heats of hydrogenation of all of the isomeric linear alkynes containing from six to ten carbons have been measured in hexane solution at room temperature. They were found to be systematically larger by about 4 kcal when the triple bond is at the end of the chain. For the remaining isomers, the heat of hydrogenation decreases further slightly and monotonically as the triple bond moves from the 2 position toward the center of the chain. This result is interpreted in terms of the conformational mixture present with the aid of molecular mechanics calculations.

The thermochemistry of linear monoalkynes is a good deal more interesting than its sparse literature[3-5] would indicate. The simple picture of a triple bond as two orthogonal ethylene-like π bonds is inadequate on thermochemical grounds alone. Twice the heat of hydrogenation of ethylene (-32.32 kcal/mol)[6] does not yield the heat of hydrogenation of acetylene (-75.06 kcal/mol)[3] and our present results show that a similar inequality holds for all linear alkynes up to and including the decynes. Moreover, Dewar[7] has pointed out that triple bonds do not behave chemically as double bonds do, e.g., in their inability to add bromine under mild conditions; nor is their electron affinity comparable to that of the olefins.[8] For a review, see ref 9.

The stability of a triple bond is known to vary with its location in the chain.[9-13] Isomerization can be brought about by treatment with base under suitable conditions. Thus, with potassium hydroxide at 175 °C, 2-pentyne is found to predominate over the 1 isomer in a ratio of 7:3.[11] Such an isomerization takes place via the allene,[11] and there is a certain amount of allene in equilibrium with the alkynes under basic conditions.[11,14] The amount of allene is small in the case of open-chain compounds,[11,14] but may be sizable with macrocyclic molecules.[15,16] The conjugated diene is even more stable, but it is more slowly formed, and rarely detected.[15] If a very strong base is used in the equilibration, such as sodamide, it will react with the 1-alkyne to give the salt.[12] The equilibrium is thus shifted by removal of the alkyne as the salt, and treatment with sodamide is a standard method for the isomerization of an acetylene to the corresponding 1-alkyne.[12] Equilibration studies on alkynes have been carried out, but the results are difficult to interpret. It would appear, at least under some conditions, that the more centrally located triple bond predominates over the less centrally located one. However, other reactions are going on which are destroying the alkynes, and it is unclear whether or not equilibrium is actually ever reached.

If we consider a series of alkynes, all of which can be reduced to the same alkane, the relative heats of formation are given directly by the relative heats of hydrogenation. Since the absolute heats of formation of the alkanes are generally known,[17] the heats of formation of the alkynes can be found.

While heats of hydrogenation in the gas phase

$$C_nH_{2n-2}(g) + 2H_2(g) = C_nH_{2n+2}(g)$$

would be most desirable, they have not been measured directly at 25 °C, because the alkynes in question are liquids in the standard state and the higher homologues are not even very volatile. Since Williams' early paper on hydrogenation in the liquid phase,[18] it has been clear that this is the method of choice for hydrocarbons of more than, say, five carbon atoms, for reasons of experimental feasibility. The heats of hydrogenation of alkynes in hexane solution are certainly not identical with the gas-phase values but, in the absence of the necessary heats of solution and vaporization, we estimate that they are very close, probably within experimental error. In effect, we are saying that the reaction producing an essentially infinitely dilute solution of reaction product in hexane

$$C_nH_{2n-2}(7\% \text{ in hexane}) + 2H_2(g) = C_nH_{2n+2}(\text{v dil})$$

is not thermochemically different from the gas-phase reaction above. This is reasonable on the qualitative grounds that separation of alkyne molecules from one another by going from

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