Photochromism and Thermochromism through Partial Torsion about an Essential Double Bond. Structure of the B Colored Isomers of Bianthrones

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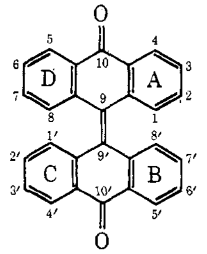
Abstract: The molecular structure of the colored labile B isomers of bianthrones was established by three methods: (1) proton nmr spectroscopy of the B isomers and of the lowest energy A forms in 1,1′-dimethylbianthrone and in the 1,1′,3,3′-tetramethyl derivative; (2) minimum strain energy computation of geometries of possible metastable isomers of bianthrones formed by torsion about the 9,9′ central double bond; and (3) analysis of the remarkable low energy shift of the first electronic transition in the B isomers. We conclude that isomer B in bianthrone proper is twisted by *ca.* 57° about the central double bond and that each of its anthrone half-molecules is planar. In 1,1′-dimethyl-substituted molecules the corresponding twist angle is *ca.* 47° but the anthrone half-molecules are significantly folded about the 9–10 axis. The observed diamagnetic shielding effects on the nmr chemical shifts of the 1-methyl protons, in both A and B forms, are in good agreement with values calculated from geometries computed by the strain energy minimalization method. The proposed structures correlate quite well with the known chemical properties of the B isomers.

We wish to report the first direct determination of the molecular structure of the B photoisomers[1] observed in bianthrone (I, Figure 1a) and in its derivatives.[3] Our experimental and computational results indicate that photoisomers B are best described as composed of two anthrone moieties highly twisted about the axis of the central (9–9′) double bond. In the presence of bulky substituents at the 1,1′ (or 1,8′) atoms or when a benzene ring is fused across the 1,2 positions, each anthrone moiety is folded about its 9–10 axis (Figure 1c and 1d), whereas in the case of bianthrone itself the anthrone moieties are planar (Figure 1b).



I

The possibility that the color changes in bianthrones are due to different extents of twisting about the 9–9′ bond has been considered by several authors.[3,5] However, due to the complexity of the problem and because of lack of suitable experimental methods it could not be determined whether this or some entirely different suggestion is the valid one.[3,5]

It has been known for some time that the colored labile modification of bianthrones which is responsible for thermochromism[5] is identical with the photochromic B isomer.[6] Thus our work solves an enigma which has puzzled chemists for over 60 years since thermochromism in bianthrones was first described by Meyer.[7]

We base our conclusions on (a) proton nmr measurements at low temperatures, (b) calculations of minimum strain energy conformations, and (c) molecular orbital calculations of electronic excitation energies.

a. Low Temperature Proton Nmr Measurements. The low temperature proton nmr spectra of the C photoisomers of 1,1′-dimethylbianthrone (II) and of 1,3,1′,3′-tetramethylbianthrone (III) have been reported previously[4] and served to establish that the C isomers have a cyclic structure (Figure 1e) analogous to that of the 4a,4b-dihydrophenanthrenes.[8] However, the experimental techniques used in the latter study allowed a conversion of at most 15% to the B isomer of III to be achieved at concentrations necessary for nmr work.[4] The nmr spectra obtained under such conditions (*cf.* Figure 3B of ref 4) were hardly adequate for the present purpose.

We have since improved considerably the photoconversion method. By the irradiation of solutions of II or III in CD_2Cl_2 or $CDCl_3$–CS_2 at 183°K with light of wavelength longer than 380 mμ, we achieve simultaneous decomposition of C and almost complete conversion into B. The 90-Mc proton nmr spectra of II and III and of their B isomers were measured in the FT or CW-CAT mode on a Brucker spectrometer and are shown in Figure 2 (A, B, and C). All the signals due to the B isomers (broken lines) revert to those of the A forms on increasing the temperature. The most salient features of the spectra of

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[1] We make use here of the nomenclature of Kortüm.[2] A = lowest energy form. The photostable isomer with $\lambda_{max} \sim 650$ mμ observed in all bianthrone and dixanthylidene derivatives is denoted as the B isomer. The photolabile C isomer (Figure 1e) has absorption maxima at *ca.* 550, 480, and 450 mμ and has been thus far observed only in bianthrones and dixanthylidenes substituted with two methyl groups at the 1 and 1′ positions.[2-4] Throughout this paper disubstitution at the 1,1′ or 1,8′ positions is not distinguished because of the possibility of rotation about the 9–9′ bond in the excited state.

[2] G. Kortüm and H. Bach, *Z. Phys. Chem.* (*Frankfurt am Main*), **46**, 305 (1965).

[3] For a recent survey of the photochemistry of bianthrones see T. Bercovici, R. Korenstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, **24**, 531 (1970).

[4] R. Korenstein, K. A. Muszkat, and E. Fischer, *Helv. Chim. Acta*, **53**, 2102 (1970).

[5] For a review on thermochromism see J. H. Day, *Chem. Rev.*, **63**, 65 (1963).

[6] Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, 629 (1953).

[7] H. Meyer, *Chem. Ber.*, **62**, 143 (1909); *Monatsh. Chem.*, **30**, 165 (1909).

[8] K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).

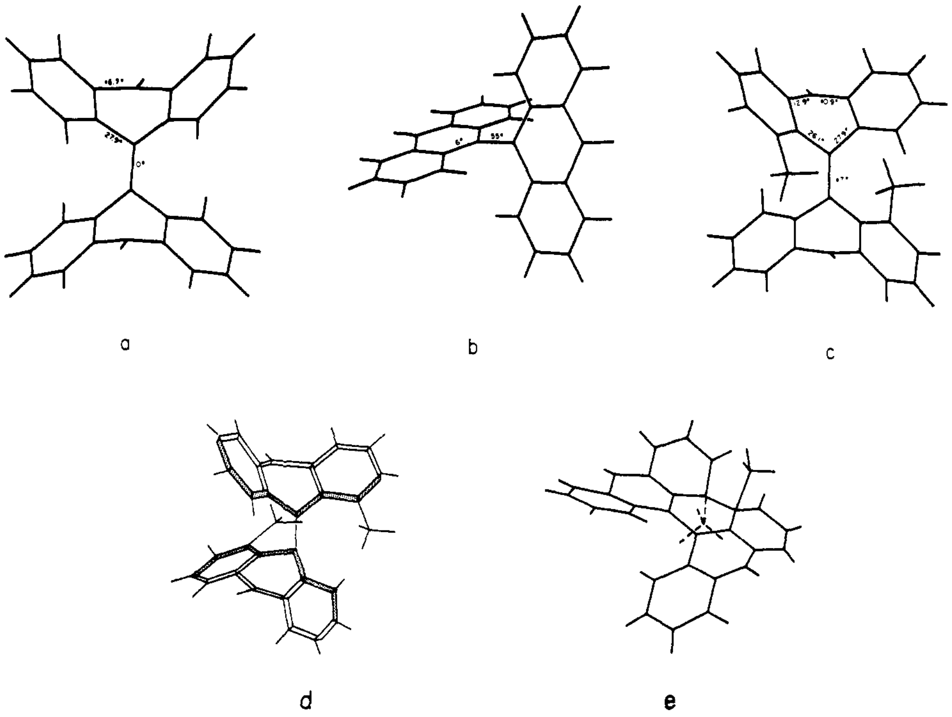

Figure 1. (a–d) Minimum strain energy conformations of: a, form A in bianthrone; b, form B in bianthrone; c and d, form B in 1,8′-dimethylbianthrone (the dihedral angles whenever significantly different from 0 or 180° are inscribed along the bonds): (e) Nonrefined model of form C in II or III.

the B forms which support the twisted model (Figures 1b, 1c, and 1d) are as follows. 1. No new signals are observed in the region 2.7–7.2 ppm (II) or 2.5–7.1 ppm (III). Therefore one can deduce that the B forms are not valence isomers of the parent bianthrones. 2. The signals due to the 1- and 1′-methyl groups of II and of III (at 1.38 and at 1.27 ppm, respectively[9]) undergo in the B forms a large downfield shift to 2.59 and 2.39 ppm, respectively. Smaller downfield shifts are also evident for the signals of the aromatic protons. These downfield shifts indicate that the process A → B removes the significant diamagnetic shielding in A of the 1-methyl protons by the opposite benzene ring (ring B, I).

The chemical shift values of the 1-methyl protons in the B forms of II and of III are usual values for aromatic methyl protons. These values are subsequently assumed to be free from any additional shielding effect of neighboring aromatic rings.

A rough estimate of the change in diamagnetic shielding for process A → B (assuming the twisted structure, Figure 1c and d)[10] was obtained from the ring current model of Johnson and Bovey.[11] According to this model the diamagnetic shielding of a proton by a benzene ring is a function of two geometrical factors: the distance between the proton and the sixfold axis (ρ) and the distance between the proton and the plane of the ring (z). For A we assumed the *folded* geometry found by Harnik and Schmidt,[12] Figure 1a, and further refined by our method (section b). For B we used the minimum strain energy *twisted-folded* geometry (Figures 1c and 1d) calculated by the procedure of paragraph b. Considering only the interaction of 1-CH$_3$ protons with ring B (see I) we estimated that process A → B results in a change in ρ from 0.83 to 3.82 Å and a change in z from 2.88 to 2.26 Å. Thus the 1-methyl protons are transferred by this process from a region of strong shielding (in A) to a region of weak or zero shielding (in B). The estimated corresponding shielding values amount to 1.60 ppm for A and to 0.07 ppm for B. The deviations of the calculated shielding change of 1.5 ppm from the observed values (1.1 and 1.2 ppm) are not unreasonable considering the known performance of the model[11] and the uncertainty in the conformation calculation.

b. Calculation of Minimum Strain Energy Conformations. The molecular geometries of the B isomers as well as refined geometries of the A forms were obtained by a program for computing minimum strain energy conformations.[13] In several respects our program is similar to the one described by Wiberg.[14,15] The

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[9] Results obtained using the shift reagent Eu(fod)$_3$ [*cf.* R. v. Ammon and R. D. Fischer, *Angew. Chem. Int. Ed. Engl.*, **11**, 675 (1972)] confirm the previous[3,4] assignment of proton nmr signals (in ppm) for III: δ^{TMS} H-8,8′ (d, 6.88), H-6,6′, H-7,7′ (t, 7.1, 7.34), H-5,5′ (d, 7.92), H-4,4′ (s, 7.67), H-2,2′ (s, 6.81).

[10] A sandwich form, in which the two anthrone halves are parallel and superimposed one on top of the other, could possibly explain the nmr results but has to be disregarded for other reasons (see below).

[11] (a) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); (b) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 64.

[12] E. Harnik and G. M. J. Schmidt, *J. Chem. Soc.*, 3295 (1954).

[13] For a review on calculations of strain energy conformations see J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).

[14] K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965).

[15] This program will be described in greater detail elsewhere. The following strain energy functions were used (angles in degrees, energy in kcal/mol). Nonbonded interactions: set III of Williams.[16] All nonbonded interactions (excluding the 1–3) were considered. Bond angle (θ) bending energy: $0.0259\ (\theta - \theta_0)^2$.[17] Torsional energy (angle θ): $64A \sin^2 \phi + 2.5B(1 - \cos 2\phi)$,[18] where A and B are the respective double and single bond characters ($A + B = 1$). Bond stretching force constant values were taken from Wilson, Decius, and Cross.[19] The geometries calculated by this program for 4a,4b-dihydrophenanthrene and for *cis*-stilbene agree closely with results obtained by a different method.[20,21]

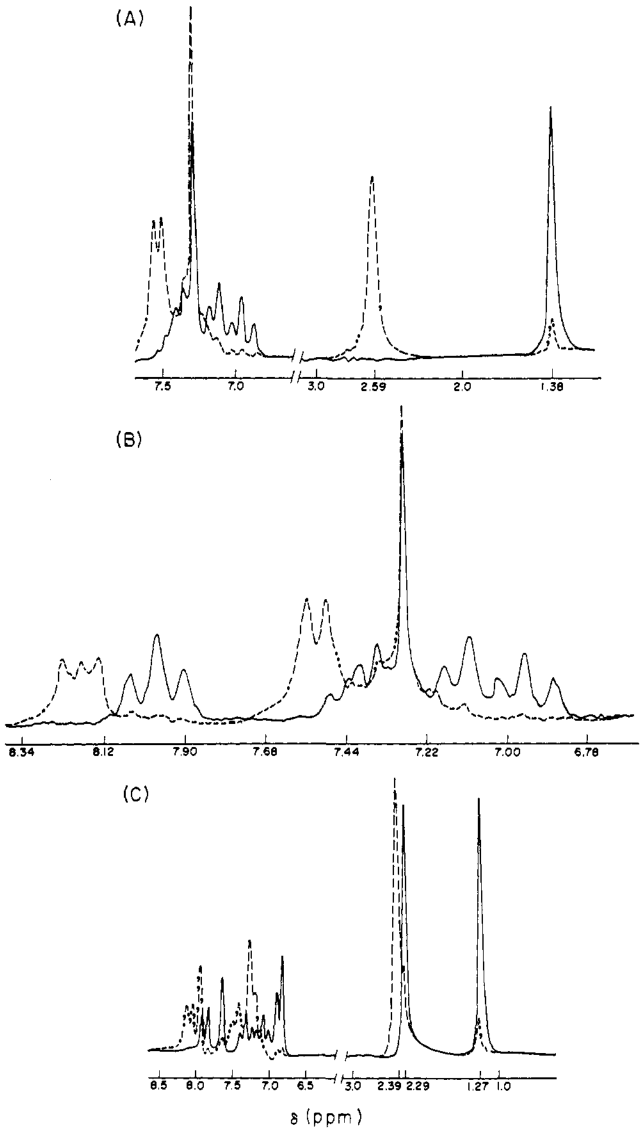

Figure 2. The 90-Mc proton nmr spectra of the A and B modifications of dimethyl-, and of tetramethylbianthrones at 183°K: full curves, A forms; broken curves, B forms. Parts A and B (II) 1.2×10^{-2} M in CS_2-$CDCl_3$, 1:2. Part C (III) 2.3×10^{-2} M in CD_2Cl_2. Measurement modes: in A and B CW-CAT, in C FT.

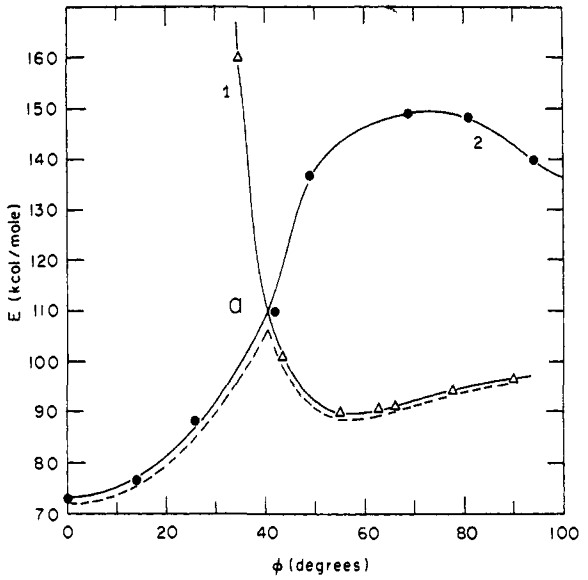

Figure 3. Strain energy potential curves for torsion about the 9-9′ bond in bianthrone: curve 1, planar form; curve 2, folded form (see text). a is the crossing point (transition state). The broken curve indicates a possible path for the thermal process B → A.

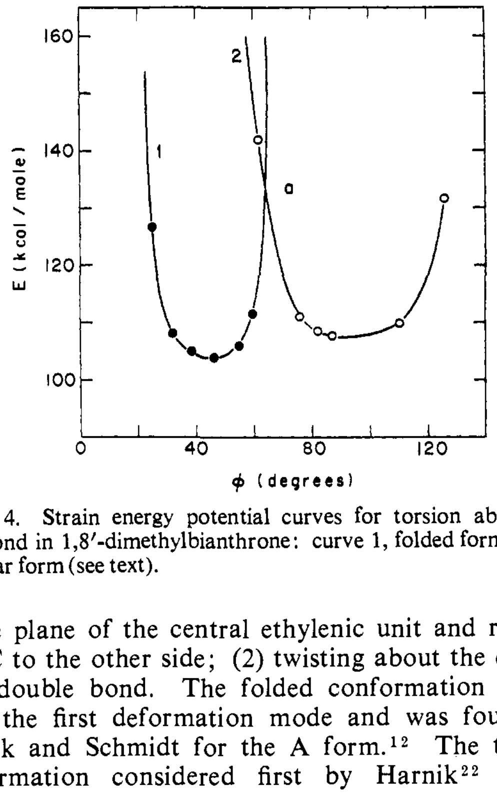

Figure 4. Strain energy potential curves for torsion about the 9-9′ bond in 1,8′-dimethylbianthrone: curve 1, folded form; curve 2, planar form (see text).

value of the 9-9′ twist angle (φ) was imposed as an external constraint and for each value of this angle several hundred iterative searches were carried out. The search was discontinued when the lowering in strain energy became less than 0.5 kcal/mol per 100 iterations. The starting trial atomic coordinates were obtained from Dreiding models.

The decisive factor which determines the geometry assumed by the conformers of bianthrone is the way in which the strong steric hindrance between the 1 and 8′ positions is relieved. This steric hindrance can in principle be minimized by two mechanisms: (1) folding of the two anthrone units about the 9-10 axis so that rings A and D are displaced to one side of the plane of the central ethylenic unit and rings B and C to the other side; (2) twisting about the central 9-9′ double bond. The folded conformation results from the first deformation mode and was found by Harnik and Schmidt for the A form.[12] The twisted conformation considered first by Harnik[22] results from the second mode. Severe steric hindrance may require the participation of both deformation modes and leads to the twisted-folded conformation assigned in the present paper to the B form of 1,8′-disubstituted bianthrones.

The following results of our calculations are summarized in Figures 3 and 4.

For a given value of φ, bianthrone and derivatives unsubstituted at the 1,1′,8,8′ positions are found to exist in principle in two different conformations: (1) folded form, in which both anthrone moieties are folded about the 9-10 axis; (2) planar form, in which

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(16) D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).

(17) W. Schmidt, Ph.D. Thesis, ETH, Zürich, 1970.

(18) A. I. Kitaigordsky and V. G. Dashevsky, *Tetrahedron*, **24**, 5917 (1968).

(19) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, Chapter 8.

(20) A. Warshel and A. Bromberg, *J. Chem. Phys.*, **52**, 1262 (1970).

(21) A. Warshel, *J. Chem. Phys.*, in press.

(22) E. Harnik, *J. Chem. Phys.*, **24**, 297 (1956).

the anthrone moieties are planar (Figure 1b). In Figure 3 we show the strain energies of these two forms *vs.* ϕ, the 9–9′ bond twist angle. For ϕ values below 40° the folded form is the more stable (Figure 3, curve 2), while for $\phi > 40^\circ$ the planar form is favored (Figure 3, curve 1). In addition to the absolute minimum at $\phi = 0^\circ$ (form A) there is a local minimum for the planar form at $\phi \backsim 57^\circ$, which we presently identify with form B in molecules *unsubstituted at the 1,1′,8,8′ positions.*

The observed strain energy difference between forms B and A, $E_B - E_A$, amounts to *ca.* 5 kcal/mol.[3,5] As our potential functions were not calibrated with regard to energy we consider the calculated value $E_B - E_A = 17$ kcal/mol as indicative only of the expected trend.

The activation energy E_a for the process B → A may be roughly deduced from Figure 3 as being equal to the energy required to reach the intersection between the potential curves for the planar and for the folded conformations (point a), starting with form B at $\phi \backsim 57^\circ$. The value thus obtained amounts to *ca.* 20 kcal/mol. The observed values for bianthrone and various derivatives fall within the range of 13–15 kcal/mol.[23,24]

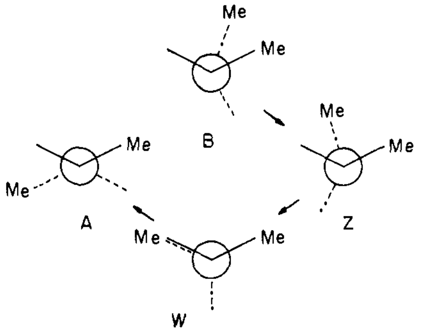
The potential curves for twisting about the 9–9′ double bond in molecules *substituted at the 1 and 1′ positions* are described in Figure 4 for the particular case of 1,1′-dimethylbianthrone; curve 1 represents the strain energy of the folded form. We tend to identify this form at its geometry proper to the energy minimum ($\phi = 47^\circ$) with the *B form of molecules substituted at 1,1′ positions.* This conformation is described in Figures 1c and 1d and was generated by forming first the *cis*-1,8′-dimethylbianthrone and then twisting by 230° about the 9–9′ double bond.

Curve 2 (Figure 4) represents a planar modification with a strain energy minimum at *ca.* 90°. This form is predicted to be paramagnetic (see below). Several previous esr investigations have shown that B is not paramagnetic.[3] Esr experiments carried out within the context of the present study lead to the same conclusion about D, the high viscosity precursor of B.[3] Therefore the 90° modification of curve 2 does not properly describe either B or D. However, it could probably fit the triplet form of bianthrones.[3]

In addition to these two local minima, we find that there are two true minima as expected. One is the trans A form (*i.e.*, methyl groups at the 1,1′ positions, $\phi = 0^\circ$). The other is the cis A form (methyl at the 1,8′ position, $\phi = 20^\circ$). Both forms have a folded structure. Several other local minima were observed at much higher energies.

An interesting property of the present calculation is the considerable stability with respect to interconversion between planar and twisted forms. As a result both forms may be initially optimized independently for any given value of constraint ϕ. Obviously after a sufficient number of iterations the higher energy form converts to the lower energy form.

The present investigation also throws considerable light on the molecular path of thermal process B → A. We mentioned previously that the activation energy for this process is approximately constant irrespective of the presence or absence of bulky substituents in the proximity of the 9–9′ double bond. Thus the B forms of bianthrone, and of the 1,1′- and 3,3′-dimethyl, 3,3′-dibromo, 1,1′-dimethoxy, 1,1′-difluoro, and 1,2,1′,-2′-dibenzo derivatives all have activation energies in the range of 13–15 kcal/mol.[23,24] This value is constant despite obvious differences in steric hindrance as far as simple rotation about the 9–9′ double bond is concerned had the two anthrone moieties been planar. This situation requires a reaction path not involving too high steric interactions. One possible sequence is described in the following scheme using Newman projections along the 9–9′ bond.



The first step (B → Z) involves inversion of the folding sense of one anthrone system and the other step (Z → W) involves motion of the substituent at position 1 past the nearby hydrogen at position 8′. A large enough extent of folding about 9–10 and 9′–10′ axes in Z and in W could prevent large steric repulsions.[25]

c. Molecular Orbital Calculations of Electronic Excitation Energies. Combined with the nmr and minimum strain energy conformation studies described in parts a and b the effects of the transitions A → B on the electronic spectrum provide a third powerful indication about the molecular structure of the B modification. The process A → B results in a shift in the energy of the first absorption band from *ca.* 25,000 to *ca.* 16,000 cm^{-1}. Historically this was the first evidence that pointed out the possibility of a twisted structure for the B isomers.[22,26]

The simplest analysis of the effect which also has the advantage of providing a clear physical picture is based on a HMO-ZDO treatement of a perturbed ethylene system. According to this picture the first electronic transition in bianthrone is considered as localized in the central double bond region. The rest of the molecule is considered as a perturbation[27] which reduces the value of the resonance integral β_0 from its value in ethylene to its apparent value in form A of bianthrone, β_0'. β', the effective resonance integral, is proportional to the value of $S_{\pi,\pi}$, the 2pπ–2pπ overlap integral between C_9 and $C_{9'}$, and therefore

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[23] T. Bercovici and E. Fischer, *Israel J. Chem.*, 7, 127 (1969).

[24] L. J. Dombrowski, C. L. Groncki, R. L. Strong, and H. H. Richtol, *J. Phys. Chem.*, 73, 3481 (1969).

[25] Following the suggestion of a referee we have considered the quantitative aspects of this path. Preliminary strain energy calculations show the presence of local minima corresponding to Z and to W.

[26] (a) W. T. Grubb and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 72, 419 (1950); (b) G. Kortüm, W. Theilacker, H. Zeininger, and H. Elliehausen, *Chem. Ber.*, **86**, 294 (1953); (c) G. Kortüm, *Angew. Chem.*, 70, 14 (1958).

[27] We have calculated both the extended Hückel[28] and MINDO/2[29] wave functions for forms A and B of bianthrone. The values of the AO coefficients of the upper occupied and of the lower unoccupied MO confirm this assumption.

[28] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[29] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

depends on cos ϕ according to

$$\beta' = \beta_0' \cos \phi \qquad (1)$$

The excitation energy of such a perturbed and twisted[30] ethylene unit is given by

$$E = -2\beta_0' \cos \phi \qquad (2)$$

This relationship can be used for obtaining a first and rough estimate of the torsional angle in the B isomers. With $E_A = 25{,}000 \text{ cm}^{-1}$, $E_B = 16{,}000 \text{ cm}^{-1}$, and $\phi_A = 0°$ we obtain a value of $\phi_B = 50°$ (A and B refer to the two forms), in good agreement with the values from the strain energy minimalization.

This conclusion is essentially unchanged by proceeding to a model that considers all the π electrons and electron–electron interactions. The two curves of Figure 5 describe the dependence of the first singlet and first triplet excitation energies on the 9–9′ twist angle, ϕ. These curves were calculated by a π-SCF-LCAO-CI-MO method,[31] using our minimum strain geometries. The calculated decrease in singlet excitation energies for process A $\rightarrow$ B amounts to 0.8 eV for bianthrone itself ($\phi_B = 57°$, planar) and to 0.5 eV for 1,1′-substituted bianthrones ($\phi_B = 47°$, folded). The first triplet excitation energies (lower curve) limit rather severely the possible ϕ_B values to below 70°, as above this value the ground state has a triplet configuration. Thus, molecules twisted by more that 70° in the 9–9′ bond would necessarily exhibit paramagnetism. This general result effectively rules out the earlier conclusion of several authors[5,26a,c,32] that the B isomers have a perpendicular structure.

As mentioned above, the sandwich model described in ref 10 is compatible with the nmr spectrum of isomer B in II or III. However, this model is completely unable to account for the low energy of the first electronic transition in B. The extended Hückel calculation indicates that in this model the predicted shift of the first-electronic transition (0.15 eV) is entirely negligible.

d. Correlation with Chemical Reactivity. The twisted model accounts fully for the known chemical[3,4] and electrochemical[33] properties of the B isomers. The B isomers are formed in strictly monomolecular processes.[3,4] In bianthrone, B does not undergo dehydrogenation by either molecular oxygen or by atomic iodine and is completely light stable.[3,4] This relative stability effectively rules out any cyclic structure of the 4a,4b-dihydrophenanthrene type.[4,8,34,35]

The B isomer of bianthrone is formed in the electrolytic oxidation of dianthranol.[33] The electrochemical reduction of B to dianthranol has a much higher rate and a considerably lower overpotential than that of A.[33] From these results Grabowski and Balasiewicz[33] were able to infer that B in bianthrone has a geometry similar to that of dianthranol, *i.e.*, that it is twisted about the 9–9′ bond.

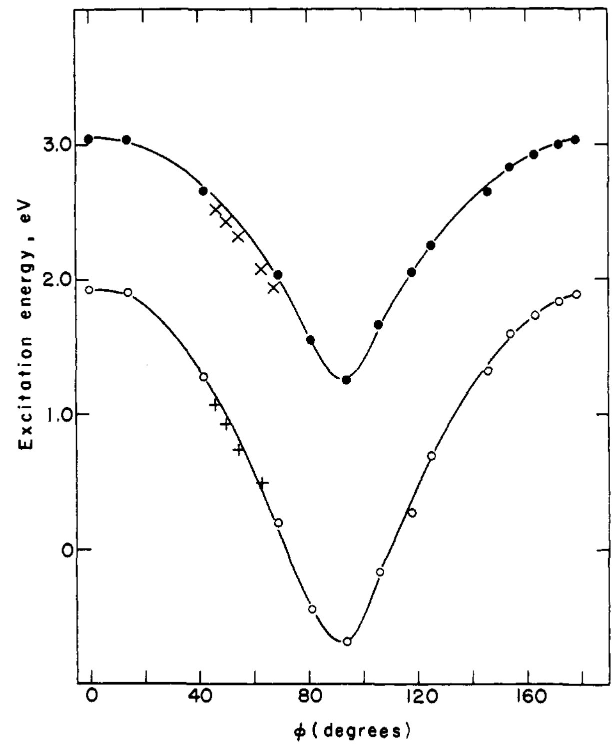
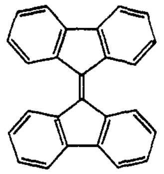


Figure 5. Calculated excitation energies *vs.* the 9–9′ torsion angle in bianthrone: upper curve, first singlet excitation energies; lower curve, first triplet excitation energies. Points denoted by crosses (×) refer to folded geometries. All other points refer to planar geometries (see text).



IV

In conclusion we would like to point out that torsion about the double bond (with its concomitant electronic effects) appears to be a general deformation mode particularly effective in reducing steric hindrance in strongly hindered ethylene derivatives. As shown in the present work this deformation occurs in bianthrones (and in dixanthylenes) only in their metastable isomers. Whenever folding about the symmetry plane of a half-molecule is not feasible, as in dibiphenylene (IV) and in its more sterically hindered derivatives, a large extent of torsion occurs in the most stable ground state conformation. This is clearly borne out by crystallographic[36] and by electronic structure–electronic spectra investigations.[37–39]

Acknowledgment. We are greatly indebted to Professors E. Fischer and M. D. Cohen (Rehovot), E. Heilbronner (Basel), H. Stegemeyer (Berlin), and H. Morrison (Lafayette) for helpful discussions on several aspects of this work.

(30) For the MO treatment of twisted ethylene see R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

(31) For parametrization and original references see A. Bromberg and K. A. Muszkat, *Tetrahedron*, **28**, 1265 (1972).

(32) S. L. Matlow, *J. Chem. Phys.*, **23**, 152 (1955).

(33) Z. R. Grabowski and M. S. Balasiewicz, *Trans. Faraday Soc.*, **64**, 552 (1968).

(34) (a) A. Bromberg and K. A. Muszkat, *J. Amer. Chem. Soc.*, **91**, 2860 (1969); (b) A. Bromberg, K. A. Muszkat, and E. Fischer, *Israel J. Chem.*, **10**, 765 (1972).

(35) T. Knittel, G. Fischer, and E. Fischer, *J. Chem. Soc., Chem. Commun.*, 84 (1972).

(36) (a) D. O. Vor der Brück, private communication; (b) N. A. Bailey and S. E. Hull, *J. Chem. Soc. D*, 960 (1971).

(37) H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **73**, 619 (1969).

(38) G. Seger, Ph.D. Thesis, Technical University, Berlin, 1971.

(39) NOTE ADDED IN PROOF. Inclusion of all doubly excited configurations involving the four lowest unoccupied MO's and the four highest occupied MO's in the π-SCF-LCAO-CI-MO calculations[31] affects only to a very limited extent the relative lowering in the energy of the first electronic transition produced by torsion of the 9,9′ bond by angles lower than 50°: G. Seger and K. A. Muszkat, unpublished results.