J. Org. Chem. 1992, *57*, 1883-1887

Molecular Conformations of 9,9′-Biantryl, Di-9-anthrylmethane, and Some Related Twisted Anthracene Derivatives

Hans-Dieter Becker,* Vratislav Langer,[†] Joachim Sieler,[‡] and Hans-Christian Becker

Departments of Organic and Inorganic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden

Received September 5, 1991

The molecular conformations of 9,9′-bianthryl (1), its 10,10′-diphenyl derivative (2), 9-*p*-tolylanthracene (3), and 9,10-diphenylanthracene (4) have been investigated by X-ray diffraction. The dihedral angle between the two aromatic ring systems in crystalline 1, in which the asymmetric unit consists of two discrete molecules, was found to be 74.65 (4) and 81.76 (5)°, respectively. In 2, the two anthracene moieties are at an angle of 87.42 (4)°, and the phenyl rings are twisted out of the plane of the adjacent anthracene by 73.2 (1) and 78.1 (1)°. The corresponding torsion angle between the two aromatic ring systems in 3 is 79.59 (8)°. In centrosymmetric 9,10-diphenylanthracene (4), the phenyl rings deviate from coplanarity with the anthracene ring system by 67.63 (5)°. Separating the two anthracene π-systems of 9,9′-bianthryl by a methylene group increases steric congestion, as was established by X-ray diffraction analysis of di-9-anthrylmethane (5). Its molecular geometry is characterized by a 2-fold axis of symmetry, and the two anthracene π-systems are in an orthogonal arrangement. Intramolecular hydrogen–hydrogen distances in 5 are as short as 1.93 (3) Å, and π-orbital interaction was found to be topologically facilitated by a contact distance of 2.601 (2) Å between the 9- and 9′-carbon atoms. By contrast, in 9-(9-anthrylmethylidene)-9,10-dihydroanthracene (6), which formally derives from 5 by a 1,5-hydrogen shift, the closest intramolecular hydrogen–hydrogen contact is 2.28 (6) Å. Relief of steric strain derives from folding of the dihydroanthracene moiety by 39.0 (2)°.

Introduction

The molecular geometry of 9-arylanthracenes is of photochemical and photophysical interest because coplanarity of the anthracene and the aryl substituent π-systems is precluded due to intramolecular repulsions involving the hydrogen atoms in the 1/8 positions of the anthracene. Consequently, π-orbital conjugation will be impaired, and deviations from molecular planarity are borne out in electronic absorption and emission spectra. In particular, the fluorescence spectra of nonplanar conjugated bichromophoric compounds, characterized by large Stokes shifts, are indicative of differences between the geometry of the ground state and that of the more planar emitting excited state.[1-3] The molecular structures of 9-anthryl-substituted ethylenes such as cis–trans isomeric 9-styrylanthracenes and various 1,2-di-9-anthrylethylenes in the crystalline state have been established by X-ray diffraction, and those findings suggest that energetically favorable ground-state conformations generally are associated with dihedral angles of 55–60° between the planes of linked π-systems and that the magnitude of the angle is governed by van der Waals contact distances of about 2.3 Å between spatially proximate hydrogen atoms.[4]

In photophysical context, 9,9′-bianthryl (1) represents a nonplanar 9-arylanthracene of unique properties insofar as its fluorescence from the locally excited state is observed in nonpolar solvents, while polar solvents induce a red-shifted emission which arises from a twisted intramolecular charge transfer (TICT) state, whose formation is associated with a change of the torsion angle about the central aryl–aryl bond.[5] As for the ground-state molecular geometry of 9,9′-bianthryl, magnetic measurements in solution are in agreement with a dihedral angle of 62 ± 5° between the planes of the two aromatic moieties,[6] and theoretical calculations for the ground state of 1 derive at a torsion angle of 67°.[7] However, fluorescence measurements on 9,9′-bianthryl generally are based on a ground-state conformation in which the two anthracene moieties are orthogonal to each other, and, for the molecular geometry of the first excited singlet state, the dihedral angle between the two anthryl groups has been determined most recently to be 70.8°.[8] Previously, angles of 67 and 78° had been reported for the geometry of the fluorescent state.[9,10] In conjunction with photochemical studies on linked bichromophoric anthracenes, we have now investigated by X-ray diffraction the molecular structures of crystalline 9,9′-bianthryl (1),[11] its 10,10′-diphenyl derivative (2), 9-*p*-tolylanthracene (3), and 9,10-diphenylanthracene (4). Moreover, for comparison purposes, we have established the conformations of di-9-anthrylmethane (5) and its structural isomer 6.

Results and Discussion

The asymmetric unit of 9,9′-bianthryl turned out to comprise two independent molecules (**1a**; **1b**), which noticeably differ in their conformations. Thus, the dihedral angle between the two 9-anthryl groups is 74.65 (4)° in **1a** and 81.76 (5)° in **1b** (the numbers in parentheses are standard deviations). Intramolecular contact distances involving the hydrogen atoms at the anthracene positions 1,1′ and 8,8′ are 3.11 (3) and 3.19 (3) Å in **1a** and 3.09 (3) and 3.31 (3) Å in **1b** (see Figure 1). These distances are

---

[†] Department of Inorganic Chemistry.

[‡] Visiting Scientist from Universität Leipzig, Germany.

(1) Becker, H.-D. *Adv. Photochem.* **1990**, *15*, 139 (Volman D. H., Hammond, G. S., Gollnick, K., Eds.); Wiley & Sons Inc.: New York) and references cited there.

(2) Castel, N.; Fischer, E.; Bartocci, G.; Masetti, F.; Mazzucato, U. *J. Chem. Soc., Perkin Trans 2* **1985**, 1969.

(3) Bhattacharyya, K.; Chattopadhyay, S. K.; Baral-Tosh, S.; Das, P. A. *J. Phys. Chem.* **1986**, *90*, 2646.

(4) Becker, H.-D.; Patrick, V. A.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 2215. Becker, H.-D.; Hansen, L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 1557.

(5) Rettig, W. *Angew. Chem.* **1986**, *98*, 969; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.

(6) Cheng, C. L.; Murthy, D. S. N.; Ritchie, G. L. D. *J. Chem. Soc., Faraday Trans. 2* **1972**, 1679.

(7) Hofmann, H.-J. *Z. Chem.* **1975**, *15*, 76.

(8) Subaric-Leitis, A.; Monte, Ch.; Roggan, A.; Rettig, W.; Zimmermann, P.; Heinze, J. *J. Chem. Phys.* **1990**, *93*, 4543.

(9) Yamasaki, K.; Arita, K.; Kajimoto, O.; Hara, K. *Chem. Phys. Lett.* **1986**, *123*, 277.

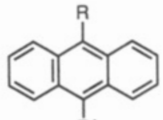
(10) Khundkar, L. R.; Zewail, A. H. *J. Chem. Phys.* **1986**, *84*, 1302. Cf. also: Mataga, N.; Yao, H.; Okada, T.; Rettig, W. *J. Phys. Chem.* **1989**, *93*, 3383 and references cited there.

(11) An X-ray diffraction study has previously been performed on a crystalline inclusion compound of benzene with 9,9′-bianthryl. The torsion angle for bianthryl has been stated to be 85.5°. Cf. Weber, E.; Ahrendt, J.; Czugler, M.; Csöregh, I. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 746.

0022-3263/92/1957-1883$03.00/0 © 1992 American Chemical Society

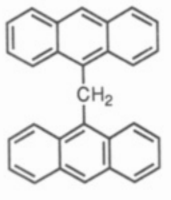
1: R = H

2: R = Phenyl

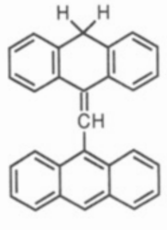


3: R = *p*-Tolyl; R′ = H

4: R = R′ = Phenyl



5



6

larger than expected, if relief of intramolecular congestion of a hypothetical planar molecule was achieved by twisting the two anthracene moieties about the 9,9′-bond just so much as to allow, in conjunction with van der Waals interactions, for optimal electronic conjugation. Computer manipulations on 9,9′-bianthryl indicate that contact distances of 2.4–2.6 Å, involving the inner peri-hydrogen atoms and spatially proximate carbon atoms, would be associated with a torsion angle of about 53°.[12]

Minor geometrical distortions in both **1a** and **1b** are apparent by deviations from planarity of the anthracene π-systems. Thus, the dihedral angles between the lateral benzene rings are 1.6 (1) and 3.47 (8)° in **1a** and 2.3 (1) and 2.9 (1)° in **1b**. Moreover, molecule **1a** differs geometrically from **1b** by its more bent molecular axis through positions 9, 10, 9′, 10′, which deviates from linearity by about 6.6 (1)°. The corresponding deviation in molecule **1b** is only 2.21 (9)°.

Further insight into the molecular topology of the 9,9′-bianthryl system was gained by the structure analysis of its 10,10′-diphenyl derivative **2**, in which the asymmetric unit comprises one molecule. Geometrical distortions in the structure of **2** are most evident in the bent molecular long axis, which deviates from linearity progressively from one end of the molecule to the other by 7.8 (2)°.[13] The dihedral angle between the planes of the anthracene moieties is as large as 87.42 (4)°, and the contact distances between the "inner" peri-hydrogen atoms are 3.38 (4) Å. As for the two phenyl rings in **2**, they are twisted out of the plane of the adjacent anthracene planes by 73.2 (1) and 78.1 (1)° (see Figure 1). Intramolecular contact distances involving the hydrogen atoms in the ortho positions of the phenyl groups on one hand, and the anthracene hydrogen atoms in positions 4,4′/5,5′ on the other, are 2.72 (4)–2.94 (4) Å.

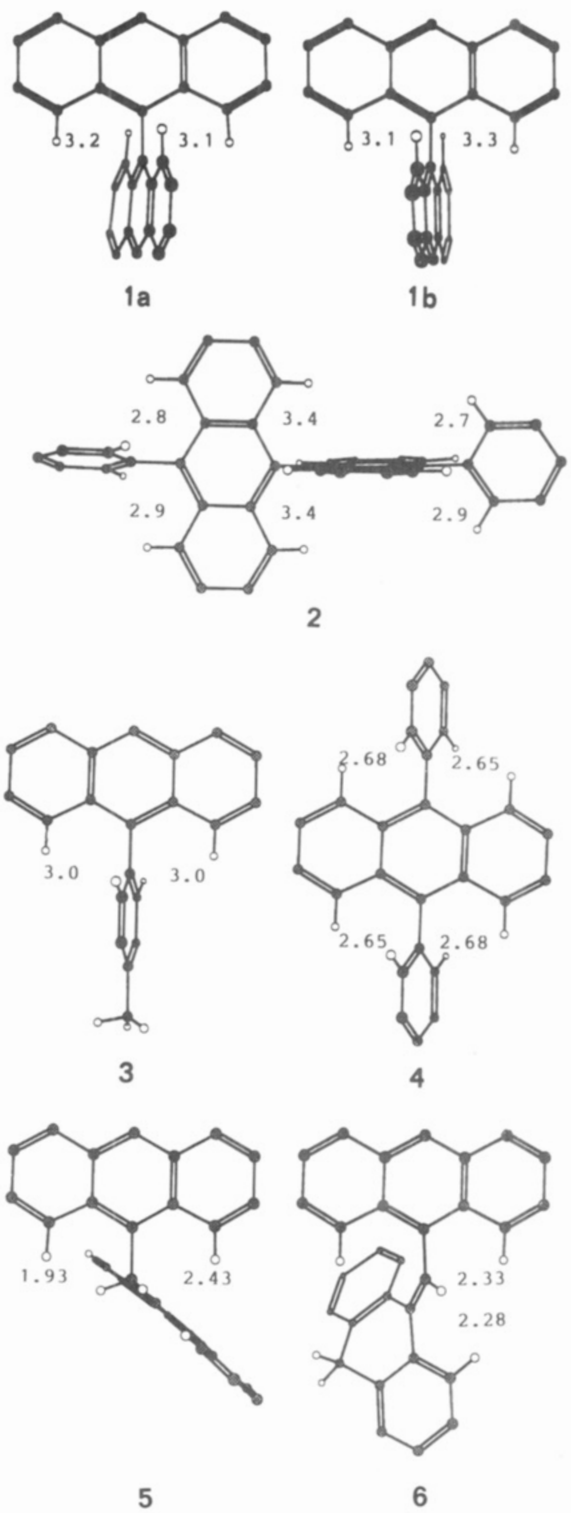


Figure 1. Perspective views of molecules **1**–**6** as present in the crystal state. In all cases, an anthracene moiety has been placed into the plane of the paper, and the inserted numbers refer to distances (in Å) between indicated proximate hydrogen atoms.

The structure analysis of **2** is of particular interest because it provides information about the conformation of the 9-phenylanthracene moiety. Magnetic measurements on 9-phenylanthracene in solution lead to a calculated torsion angle of 70 ± 6°.[6] Structural data for 9-phenylanthracene in the crystal state have not been reported in the literature, but X-ray diffraction analyses of related compounds show that the phenyl group can be twisted out of the plane of the anthracene to varying degrees. For example, in the 10-acetoxy derivative of 9-phenylanthracene, having three discrete molecules in its asymmetric unit, the torsion angles are 73, 74, and 79.7°.[14] The X-ray diffraction analysis of 9-*p*-tolylanthracene (**3**) of the present study reveals a torsion angle of 79.59 (8)° and

---

(12) The computer program used was Chem3D Plus 3.0, available from Cambridge Scientific Computing Inc., Cambridge, MA 02139.

(13) The deviation from linearity of the molecular long axis was calculated as the angle formed between the axes of the terminal phenyl rings.

(14) Roszak, A.; Borowiak, T. *Acta Crystallogr.* 1987, *C43*, 498.

Table I. Dihedral Angles between Anthryl/Aryl Planes and Anthryl–Aryl Bond Distances in 1–4

biantryl geometries:	1a	1b	2
anthryl/anthryl angle (deg)	74.65 (4)	81.76 (5)	87.42 (4)
anthryl–anthryl distance (Å)	1.502 (4)	1.497 (4)	1.501 (4)
9-arylanthryl geometries	2	3	4
aryl/anthryl angle (deg)	78.1 (1); 73.2 (1)	79.59 (8)	67.63 (5)
aryl–anthryl distance (Å)	1.493 (4); 1.489 (4)	1.498 (3)	1.488 (2)

intramolecular hydrogen atom contact distances of 3.0 Å (see Figure 1).

As for 9,10-diphenylanthracene (4), its structure has previously been investigated by X-ray diffraction of a single crystal grown from a xylene solution.[15] However, we have deemed it worthwhile to reinvestigate the molecular geometry of 9,10-diphenylanthracene as a complement to the conformational investigation of 2, since the reported range of aromatic carbon–carbon distances (1.30 to 1.48 Å) and bond angles (115.9 to 126.0°) is remarkably wide. More important, the length of 1.56 Å reported for the anthryl–phenyl bond appears far too large by comparison with the lengths of the aryl–aryl bonds found in structures 1–3 (see Table I).

The unit cell of 9,10-diphenylanthracene crystals, which were grown for this study from a dichloromethane solution containing about 20% methanol, turned out to be identical with that of crystalline 4 prepared previously.[15] The present X-ray diffraction analysis confirms that the 9,10-diphenylanthracene structure is centrosymmetric and that the phenyl rings are twisted out of the plane of the anthracene by 67.63 (5)° (see Figure 1). Intramolecular contact distances between proximate hydrogen atoms in the ortho positions of the phenyl rings on one hand, and H-1/H-8 of the 9-anthryl group on the other, being 2.65 (3) and 2.68 (3) Å, respectively, are slightly shorter than the corresponding distances found in 9-arylanthracenes 2 and 3. Carbon–carbon bond lengths of the aromatic skeletons of 4 are normal, as they range between 1.352 (3) and 1.437 (2) Å, and so are intramolecular carbon–carbon bond angles, which vary between 117.9 (2) and 121.9 (1)°. Significantly, we find that the essential bond between the phenyl group and the anthracene is not exceptionally long, but the carbon–carbon distance in question is 1.488 (2) Å. It is worth noting in this context that the lengths of the corresponding aryl–anthryl bonds in 10-bromo-1,8-diphenylanthracene, whose phenyl groups are twisted out of the plane of the anthracene by 55–56°, are 1.485 (6) and 1.486 (6) Å.[16]

In order to evaluate the topological changes brought about by separating the anthracene moieties in 9,9′-bianthryl by one methylene group, we have extended the present investigation to di-9-anthrylmethane (5). Dianthrylmethane is of interest from a photochemical point of view because it undergoes intramolecular 4π + 4π cycloaddition with relatively high quantum yield (0.15), and its ground-state geometry, in which the 9- and 9′-carbon atoms are assumed to be only 2.1 Å apart, has been suggested to be of importance for the efficiency of the reaction in the excited state.[17]

Significantly, the electronic absorption spectra of 9,9′-bianthryl and di-9-anthrylmethane are strikingly similar in shape (see Figure 2), and the comparison also reveals that the longest-wavelength absorption maximum of dianthrylmethane 5 (λ_{max} 396 nm; ε 22 000 M^{-1} cm^{-1}; in dichloromethane) is bathochromically shifted relative to that of bianthryl 1 (λ_{max} 391 nm). This finding is indicative of intramolecular interactions between spatially proximate π-systems in 5.[18] It should be noted in this context that the longest-wavelength absorption maximum of 9-methylanthracene (in dichloromethane) appears at 389 nm.

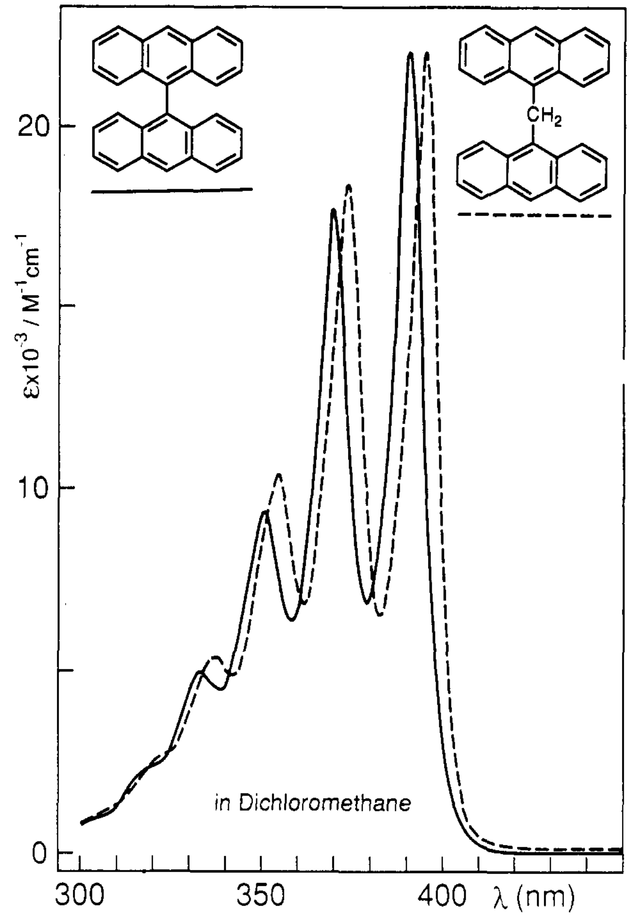


Figure 2. Electronic absorption spectra of 9,9′-bianthryl (solid line) and di-9-anthrylmethane (dashed line) in dichloromethane.

The molecular geometry of di-9-anthrylmethane in the crystal state is found to be characterized by a 2-fold axis of symmetry. The dihedral angle between the two anthracene planes in 5 is 87.83 (3)°, i.e., the aromatic π-systems are in a nearly perfect orthogonal arrangement (see Figure 1).[19] The spectroscopically indicated π-orbital interactions between the two anthracene moieties may be explicable by the C-9–C-9′ contact distance, which we find to be 2.601 (2) Å. Remarkably, the intramolecular contact distance between the hydrogen atoms of the methylene group and the hydrogen atoms of the anthracene positions 1,1′/8,8′ is as short as 1.93 (3) Å. Obviously, di-9-anthrylmethane is an overcrowded molecule in which intramolecular hydrogen–hydrogen interactions are more repulsive than they are in 9,9′-bianthryl. The length of the 9-anthryl–alkyl bond (1.522 (2) Å) is not exceptional. However, dianthrylmethane evades spatial congestion by increasing the tetrahedral angle about the anthryl–CH_2–anthryl linkage to 117.4°. Moreover, the anthracene π-

---

(15) Adams, J. M.; Ramdas, S. *Acta Crystallogr.* 1979, *B35*, 679.

(16) House, H. O.; Ghali, N. I.; Haack, J. L.; VanDerveer, D. *J. Org. Chem.* 1980, *45*, 1807.

(17) Bergmark, W. R.; Jones, G., II; Reinhardt, T. E.; Halpern, A. M. *J. Am. Chem. Soc.* 1978, *100*, 6665.

(18) For a discussion of absorption spectroscopically detectable conformational repercussions on the photochemical properties of bichromophoric anthracenes, see ref 1. Cf. also: Becker, H.-D.; Andersson, K. *J. Org. Chem.* 1982, *47*, 354. Becker, H.-D.; Patrick, V. A.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* 1985, *38*, 1417.

(19) By and large, the molecular topology of 5 resembles that of di-9-anthryl ketone: Becker, H.-D.; Langer, V.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* 1989, *42*, 603.

systems in di-9-anthrylmethane deviate markedly from planarity; the dihedral angle between the lateral rings of the anthracene moieties in **5** is as large as 5.86 (8)°.

The steric strain of di-9-anthrylmethane probably also has chemical implications. For example, reduction of di-9-anthrylmethanol with lithium aluminum hydride in the presence of aluminum chloride results in the formation of 9-(9-anthrylmethylidene)-9,10-dihydroanthracene (**6**) rather than di-9-anthrylmethane.[20] Since **6** formally differs from dianthrylmethane **5** by a 1,5-hydrogen shift which involves the sterically demanding central methylene group, we deemed it of interest to compare the structures of both isomers. The X-ray diffraction analysis of **6** shows that the contact distance involving the methylidene hydrogen and the closest aromatic hydrogen (see Figure 1) is 2.28 (6) Å, i.e., as expected for typical hydrogen–hydrogen van der Waals interactions. Relief of steric strain derives mainly from the conversion of the 9-anthrylmethyl fragment in **5** into the folded methylidene-substituted 9,10-dihydroanthracene moiety of structure **6**, in which the dihedral angle between the aromatic rings is 39.0 (2)° (see Figure 1). The vinyl group is twisted out of the plane of the anthracene π-system by 61.2 (5)°.[21] The dihedral angle between the lateral rings of the anthracene moiety in **6** is as small as 1.9°, indicating that geometrical distortions in **6** are negligible by comparison with those of dianthrylmethane **5**.

The question arises as to whether the molecular conformations of anthracene derivatives **1–6** established by X-ray diffraction can be assumed to resemble ground-state conformations existing in the absence of a constraining crystal lattice. We have addressed this problem by calculating the molecular structures of 9,9′-bianthryl, 9-phenylanthracene, and 9,10-diphenylanthracene, as well as those of di-9-anthrylmethane and its isomer **6** by applying the Chem3D Plus 3.0 energy minimization program with an implementation of the MM2 force field.[12] The results can be summarized as follows. For 9,9′-bianthryl, 9-phenylanthracene, and 9,10-diphenylanthracene, MM2 calculations lead to more than one low-energy conformation, indicating the existence of a shallow minimum or several local minima on the ground-state potential energy curve. One of the low-energy conformations of bianthryl is characterized by a dihedral angle of about 90° between the two π-systems. However, when the MM2 calculation for 9,9′-bianthryl commences with a dihedral angle set at 40°, the energy-minimized structure of bianthryl will be such as to have the two π-systems at an angle of 72° and the distances between hydrogen atoms 1/8 and 1′/8′ are 3.20 Å. Contact distances involving H-1 and the spatially proximate anthracene carbon atoms C-9, C-9a, and C-1 are 2.60, 2.76, and 3.10 Å, respectively.[22] Similar results were obtained for energy-minimized 9-phenylanthracene and 9,10-diphenylanthracene, in which the phenyl rings were found to be twisted out of the plane of the anthracene by about 72 and 75°, respectively. By and large, the dihedral angles between the planes of aromatic π-systems found by X-ray diffraction of 9-arylanthracenes **1–4** thus do fall within the range derived at by calculation.

As for "vinylanthracene" **6**, MM2 calculations lead to a conformation which closely resembles that of **6** in the crystalline state: the vinyl group is twisted out of the plane of the anthracene by 60°, and the intramolecular contact distance between proximate hydrogen atoms is 2.4 Å. Likewise, a striking resemblance between the molecular structure established by X-ray diffraction and the structure derived at by MM2 energy minimization was found in the case of di-9-anthrylmethane (**5**).

In summary, we conclude from the X-ray diffraction analyses of 9-arylanthracenes **1–4** that the intramolecular distance between proximate hydrogen atoms exceeds the typical contact distance of about 2.3 Å, i.e., the aryl substituent is twisted out of the plane of the anthracene moiety to a larger degree than found for 9-anthryl-substituted ethylenes. In 9,9′-bianthryl, the molecular topology apparently is governed by repulsive interactions between the anthracene π-system and the H1/H8 hydrogen atoms. For 9-vinyl-substituted anthracene **6**, by contrast, the magnitude of the torsion angle about the anthracene and vinyl π-systems is such as to keep intramolecular hydrogen atom contact distances within the range of typical van der Waals interactions, so that optimal conjugation of the two π-systems prevails. Finally, the X-ray diffraction analysis of di-9-anthrylmethane (**5**) reveals that separation of the two anthracene moieties in 9,9′-bianthryl (**1**) by a methylene group increases steric congestion and enhances intramolecular π-chromophore interactions, which are borne out in the electronic absorption spectrum by a bathochromic shift.

Experimental Section

Compounds **1–6** have previously been reported in the literature. The experimental descriptions given below are therefore limited to an outline of the synthetic routes chosen in the present study and to the preparation of single-crystal specimens used for the X-ray diffraction analyses.

9,9′-Bianthryl (1) was prepared from 9-anthrone by reductive dimerization in acetic acid in the presence of zinc, as described previously.[23] The needle-shaped colorless crystal sample analyzed by X-ray diffraction was obtained by slow crystallization from a mixture of dichloromethane and methanol.

10,10′-Diphenyl-9,9′-bianthryl (2). Reductive dimerization of 10-phenyl-9-anthrone (2.4 g) according to the previously reported[23] procedure afforded 0.29 g of **2** (purified by column chromatography on silica gel/dichloromethane). Compound **2** had been described in the literature to form a yellow crystalline powder (no mp <300 °C)[24,25] which melts at 390–391 °C.[26] Upon recrystallization from toluene, **2** crystallizes with two solvent molecules.[26] For the present investigation, **2** was recrystallized slowly from a dichloromethane/methanol mixture and formed nearly colorless needle-shaped crystals, which did not melt below 350 °C.

9-*p*-Tolylanthracene (3). The synthesis of **3** was accomplished as follows. Sodium borohydride (1 g) was added to a solution of 10-*p*-tolylanthrone[24] (500 mg; prepared from 10-bromoanthrone and toluene in the presence of aluminum chloride) in dioxane (10 mL), and the reaction mixture was refluxed for 10 min. The reaction mixture was then diluted with methanol

---

(20) Applequist, D. E.; Swart, D. J. *J. Org. Chem.* **1975**, *40*, 1800.

(21) From dipole moment measurements, it has been concluded that the dihedral angle between the anthracene and the ethylene moieties in 9-vinylanthracene is 60 ± 10°: Le Fèvre, R. J. W.; Ritchie, G. L. D. *J. Chem. Soc. B* **1968**, 775.

(22) Some explanatory comments about the calculated conformations may be in order. For any conformation of 9,9′-bianthryl, close contact distances always involve H-1 (H-8) and the proximate carbon atoms C-9, C-9a (C-8a), and C-1 (C-8). In an 89° conformer, the corresponding contact distances are 2.58, 3.02, and 3.56 Å, the contact distance between spatially proximate hydrogen atoms being 3.62–3.66 Å. The length of the central bond in the 89° conformer is 1.51 Å, indicating decreased resonance stabilization of the two anthryl moieties. A dihedral angle of about 55° between the two anthracene moieties would be associated with contact distances of 2.4–2.6 Å. The 72° conformer is about 0.9 kcal/mol higher in steric energy than the 89° conformer. The central carbon–carbon bond in the 72° conformer, being 1.50 Å, is in fair agreement with the crystallographic results. By and large, the increase in steric freedom about the aryl–aryl linkage is paralleled by a decrease in electronic conjugation.

(23) Becker, H.-D., Andersson, K. *J. Org. Chem.* **1981**, *46*, 5418.

(24) Barnett, E. de Barry; Cook, J. W. *J. Chem. Soc.* **1923**, *123*, 2631.

(25) Schönberg, A.; Ismail, A. F. A. *J. Chem. Soc.* **1945**, 201.

(26) Dufraisse, C.; Velluz, L.; Velluz, Mme. L. *Bull. Soc. Chim. Fr.* **1938**, *5*, 600.

(10 mL), and refluxing was continued for an additional 20 min. Subsequently, the solution was cooled to room temperature and acidified with acetic acid (10 mL) and concd hydrochloric acid (10 mL) to give a suspension which was extracted with dichloromethane. Conventional further workup of the dichloromethane solution gave a dark oily residue which was subjected to column chromatography on silica gel/dichloromethane. Tolylanthracene **3** (fast-moving fluorescent fraction) was recrystallized from dichloromethane/methanol to give almost colorless crystals (yield 100 mg) which melt at 146–148 °C (lit.[27] mp 145–147 °C).

9,10-Diphenylanthracene (4) was crystallized slowly from dichloromethane solution containing about 20% methanol.

Di-9-anthrylmethane (5) and 9-(9-anthrylmethylidene)-9,10-dihydroanthracene (6) were prepared from di-9-anthrylmethanol according to the literature.[20] Dianthrylmethane was crystallized slowly from xylene solution to give yellow needle shaped crystals. Needle-shaped crystals of **6** were obtained by slow crystallization from dichloromethane/methanol.

Structure Determinations. The structures were solved by direct methods.[28] Calculations were performed with the TEXSAN crystallographic software package of Molecular Structure Corporation.[29] All pertinent crystallographic data, including atomic coordinates, are available elsewhere in printed form.[30]

Registry No. 1, 1055-23-8; 2, 23102-67-2; 3, 23674-14-8; 4, 1499-10-1; 5, 15080-14-5; 6, 55043-37-3; 9-anthrone, 90-44-8; 10-phenyl-9-anthrone, 14596-70-4; 10-*p*-tolylanthrone, 127255-73-6; 10-bromoanthrone, 1560-32-3; toluene, 108-88-3; 2·2PhMe, 138836-10-9.

---

(27) Lown, J. W.; Aido, A. S. K. *Can. J. Chem.* **1971**, *49*, 1848.

(28) Sheldrick, G. M. *SHELXS86. Crystal Structure Solution Computer Program*, University of Göttingen, Germany, 1986.

(29) TEXSAN—TEXRAY Structure Analysis Package, Molecular Structure Corporation, 1985, The Woodlands, TX.

(30) 1a/1b: *Z. Kristallogr., New Crystal Structures*, in press. 2: *Ibid.*, in press. 3: *Ibid.*, in press. 4: *Ibid.*, in press. 5: *Ibid.*, in press. 6: *Ibid.*, in press.

Solvolytic Elimination Reactions of Tertiary α-CSNMe$_2$-Substituted Systems

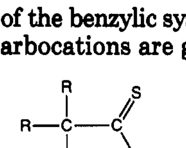
Xavier Creary,* Holia N. Hatoum, Angela Barton, and Timothy E. Aldridge

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

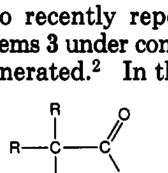
Received October 15, 1991

The tertiary benzylic α-CSNMe$_2$-substituted *p*-nitrobenzoates and trifluoroacetates of general structure Ar(CH$_3$)C(CSNMe$_2$)(OCOR), **7** and **8**, solvolyze to give exclusively elimination products H$_2$C=C(CSNMe$_2$)Ar. A Hammett study gave a nonlinear correlation. Variation in rate with solvent ionizing power was small for the unsubstituted trifluoroacetate derivative of **8**, and the β-CD$_3$ isotope effect on rate was negligible. There is, however, a large isotope effect (2.5–2.8) in formation of the elimination product when Ph(CH$_2$D)C(CSNMe$_2$)(OCOCF$_3$) solvolyzes. It is concluded that an intermediate must be involved since the product-determining step and the rate-determining step have differing isotope effects. The likely intermediate is an α-CSNMe$_2$-substituted cation (as an ion pair), despite the fact that the reaction has few characteristics of a typical E1 reaction. Tertiary norbornyl, cyclohexyl, and 2-propyl α-CSNMe$_2$-substituted systems also react to give exclusively elimination products at rates far in excess of α-CONMe$_2$ analogues. It is suggested that α-CSNMe$_2$ cations are also intermediates and that these cations undergo proton loss at an early ion pair stage. These cations are proposed to derive substantial stabilization by charge delocalization onto sulfur of the thiocarbonyl group. By way of contrast, the secondary system CH$_3$CH(CSNMe$_2$)(OCOCF$_3$), **25**, solvolyzes to give mainly a rearranged product CH$_3$CH(CONMe$_2$)(SCOCH$_3$) via a k_Δ mechanism involving neighboring thiocarbonyl participation leading to a cyclized ion.

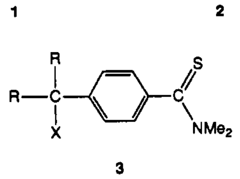
Mechanisms by which the thiocarbonyl group interacts with a cationic center has been an area of interest. In this regard we have presented a preliminary study[1] on the solvolytic reactivity of systems of structure **1**. These systems react at rates that far exceed those of the carbonyl analogues **2**. We have also recently reported on the chemistry of the benzylic systems **3** under conditions where benzylic carbocations are generated.[2] In these systems, the CSNMe$_2$ group has an amphielectronic effect, i.e., the cation derived from **3** can be stabilized or destabilized by the CSNMe$_2$ group depending on the nature of the R groups. We have suggested that the thioamide group can stabilize a cationic intermediate by a conjugative interaction as represented by **4b**. Theoretical studies support this suggestion.[3,4] To account for the variable electronic effect of the thioamide group on benzylic cations, we have also suggested that the importance of this effect is very dependent on the extent of positive charge development. We have also proposed that, in certain instances, the thiocarbonyl group can interact with a cationic center to form cyclized ions of type **5**. These assisted ionization rates are accompanied by large rate enhancements. In this paper we present full details on the solvolytic reactivity of a number of the thioamide containing systems.



1



2



3

---

(1) Creary, X.; Aldridge, T. E. *J. Org. Chem.* **1988**, *53*, 3888.

(2) Creary, X.; Aldridge, T. E. *J. Org. Chem.* **1991**, *56*, 4280.

(3) Lien, M. H.; Hopkinson, A. C. *J. Am. Chem. Soc.* **1988**, *110*, 3788.

(4) For a report on the generation of 4 (R = aryl) under stable ion conditions, see: Ablenas, F. J.; George, B. E.; Maleki, M.; Jain, R.; Hopkinson, A. C.; Lee-Ruff, E. *Can. J. Chem.* **1987**, *65*, 1800.

0022-3263/92/1957-1887$03.00/0 © 1992 American Chemical Society