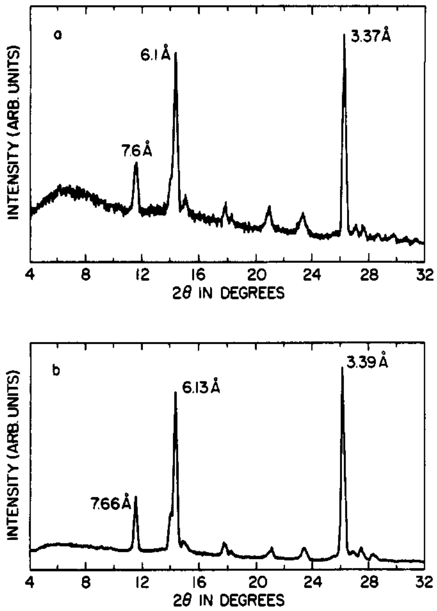

Figure 3. X-ray powder diffraction patterns of (a) **USq-1** and (b) model squaraine **2**.

ventional photoconductive squaraines exhibit flat photoresponses between 500 and ~900 nm, but the photoresponses at 400–500 nm are rather poor due to the low absorptivity. Since the output of the diode laser used in laser-addressed technologies is at ~780 nm and photoresponses beyond that are unused anyway, our approach to improve the spectral response is to engineer a 50–100 nm hypsochromic shift in the solid-state absorption of squaraine. This will enable the resulting xerographic device to have flat photoresponses from 400 to ~800 nm. On the basis of recent spectroscopic and theoretical studies, we launched an effort to synthesize unsymmetrical squaraines, **USq-1–13** where the dimethylamino group in squaraine is replaced by a less powerful, electron-releasing methoxy group. Hypsochromic shifts on both solution- and solid-state absorption are indeed obtained. Preliminary measurements on the photoconductivity of these compounds already revealed the expected improvement at 400–500 nm.

The unsymmetrical photoconductive squaraines synthesized in this work were prepared by a cycloaddition–condensation reaction sequence. By using a secondary alcohol as reaction solvent and tributyl orthoformate as an in situ homogeneous drying reagent, we have been able to suppress both secondary and side reactions, enabling these compounds to be synthesized in high chemical yields in a very short reaction time. The synthesis represents *the first general synthesis of photoconductive squaraine without using squaric acid as a precursor.* Our current effort is to extend our synthetic concept to synthesize symmetrical and unsymmetrical photoconductive squaraines with dimethylamino groups using a similar cycloaddition–condensation reaction sequence. Preliminary results are encouraging.[49]

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[49] Law, K. Y.; Bailey, F. C. *J. Chem. Soc., Chem. Commun.* **1991**, 1156.

Crystal and Molecular Structure of 10-Substituted 9-Anthracenones. Substituent Size as the Controlling Factor for the Nonplanarity of the Central Ring

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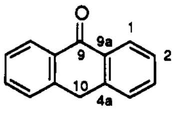
MM2 calculations for a series of 10-*R*-9-anthracenones demonstrate an increase of the folding of the central ring with increasing size of the substituent. All the substituents considered prefer the pseudoaxial position except fluorine, which prefers the pseudoequatorial orientation. The anthracenone moiety approaches planarity when the size of the substituents approaches the size of the hydrogen atom. The planar conformation for 9-anthracenone is also shown by vibrational frequency calculations to be a true potential energy minimum at the ab initio 3-21G level. X-ray structure determination shows that 10-R-9-anthracenones (R = Me, iPr, tBu, Ph, and Br) generally exhibit the structural features predicted by MM2 calculations for the isolated molecules. However, 10-Me and 10-Ph-9-anthracenones are found to be significantly less folded than calculated by MM2, the discrepancy being attributed to the crystal packing forces. Consideration of the theoretical as well as the experimental results leads to the conclusion that the parent 9-anthracenone is expected to be planar in the crystal state.

Introduction

The structure of 9-anthracenone (9-anthrone) derivatives is of interest since some of them are biologically active. However, the structure of the parent 9-anthracenone (**1**) is controversial; **1** displays structural disorder in the crystal, so the details of its crystal structure are not known.[1,2] Also, a large independent out-of-plane vibration of the oxygen atom precludes determination of whether **1** is planar or folded in the crystal.[1] The ^{1}HNMR analysis of **1** suggested an inverting nonplanar molecule in solution based on the interpretation of the long-range, spin–spin coupling constants.[3] On the other hand, earlier solution studies based on dipole moment and the Kerr constant



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[1] Flack, H. D. *Philos. Trans. R. Soc. London, Ser. A* **1970**, *266*, 561.

[2] Srivastava, S. N. *Ind. J. Phys.* **1972**, *46*, 56.

[3] Schaefer, T.; Sebastian, R.; Wildman, T. A.; Dettman, H. *Can. J. Chem.* **1982**, *60*, 2274.

0022-3263/92/1957-3286$03.00/0

analysis suggested a planar or nearly planar molecule as the lowest energy conformation for anthrone itself.[4] Similarly, recent ab initio calculations show planar 1 to be the minimum energy conformation with a low energy required for a modest folding of the molecule along the C9–C10 axis.[5]

Several crystal structures for anthracenone derivatives are known.[6-10] Depending on substitution, the central ring of the anthracenone moiety adopts planar,[7,8] boat,[6,10] or even envelope[9] conformations in the crystal state. While this confirms the sensitivity of the system to the nature of the substituents, it does not resolve the question regarding the favored conformation of 1 itself. Moreover, all of the known structures include polar substituents that introduce additional complicating factors like dipole–dipole and/or hydrogen bond interactions.

The present study of several 10-monosubstituted anthracenones allows some conclusions to be drawn about the structure of the parent 1. The substituents chosen were those expected to introduce only steric interactions so as to simplify the analysis of the results. Moreover, we are interested in comparison of the structures of anthracenones with analogous 9,10-dihydroanthracenes due to the apparent similarities in their structures. Herein we provide molecular mechanics calculations for a series of 10-R-1 derivatives together with crystal structure determinations for 10-phenyl-1 and several 10-alkyl derivatives to verify the theoretical results.

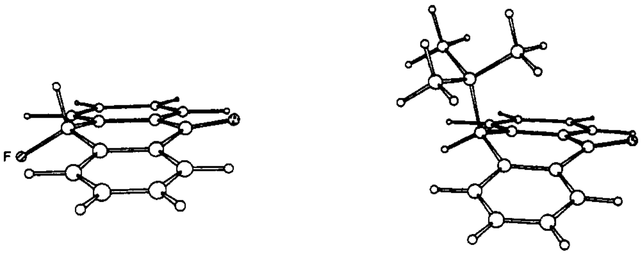
Experimental Section

Calculations. Molecular mechanics calculations were performed without any symmetry constraints using the MM2/87 program of Allinger.[11] For the substituents of lower symmetry (e.g., Et and iPr) both possible conformations were considered, and the one of lower steric energy was chosen to represent the molecule in question.

Semiempirical molecular orbital calculations were carried out using the AM1 method[12] employed in the MOPAC program package.[13] C_s symmetry constraints were employed whenever possible.

Ab initio calculations for unsubstituted 1 were performed using the GAUSSIAN 88 program package.[14] Geometry optimization was carried out within the Hartee–Fock approximation with the 3-21G basis set,[15] generally accepted as sufficient for this purpose.[16] The resulting structure was characterized by calculations of vibrational frequencies.

Materials. 10-Me-1[17] and 10-Ph-1[18] were obtained and purified by published methods since the simpler oxidation procedure below was unsuccessful giving 10-Me-10-hydroxy-1 and 10-Ph-10-hydroxy-1, respectively, as the main products.



10-F-1 10-t-Bu-1

Figure 1. MM2 optimized geometries of 10-F-1 and 10-tBu-1.

Oxidation Procedure. 10-iPr-1 and 10-tBu-1 were synthesized by sodium dichromate/acetic acid oxidation of 9-iPr-9-10-dihydroanthracene[19] and 9-tBu-9,10-dihydroanthracene,[19] respectively, according to the following procedure. Sodium dichromate dihydrate, 6.25 mmol (1.25 equiv, 1.86 g), was added in portions to a stirred solution of 5 mmol of the appropriate 9-R-9,10-dihydroanthracene (R = iPr, tBu) in 15 mL of acetic acid. Stirring was continued at room temperature, and the reaction progress was monitored by GC. After oxidation was completed (ca. 72 h) the reaction mixture was diluted with water and extracted with diethyl ether. The organic layer was separated, washed with sodium bicarbonate solution and with water, dried, and evaporated under reduced pressure to afford the anthrone in ca. 90% yield.

10-Isopropyl-9-anthracenone was obtained as colorless crystals (hexane): mp 58 °C; ^{1}H NMR ($CDCl_3$) δ 0.69 (d, 6 H, J = 6.8 Hz), 1.9–2.3 (m, 1 H), 4.12 (d, 1 H, J = 3.5 Hz), 7.2–7.6 (m, 6 H), 8.15–8.3 (m, 2 H); MS m/z (relative intensity) 236 (3), 194 (100), 165 (67), 139 (7). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40, H, 6.82. Found: C, 86.59, H, 7.02.

10-*tert*-Butyl-9-anthracenone was obtained as colorless crystals (hexane): mp 118–119 °C; ^{1}H NMR ($CDCl_3$) δ 0.79 (s, 9 H), 3.87 (s, 1 H), 7.3–7.6 (m, 6 H), 8.05–8.2 (m, 2 H); MS. m/z (relative intensity) 235 (4), 194 (100), 165 (54), 139 (5). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36, H, 7.25. Found: C, 86.49, H, 7.35.

Crystallographic data for 10-R-1, where R = Me, iPr, tBu, and Ph. Intensity data were collected on Enraf-Nonius CAD4 diffractometers using graphite-monochromated CuKα (l = 1.541 84 Å) or MoKα (l = 0.710 73 Å) radiations, and all calculations were carried out using the Enraf-Nonius MolEN programs. Intensity data were measured using ω-2Θ scans of variable rate. Data having intensities greater than $3\sigma(I)$ were used in the refinements. Data reduction included corrections for background, Lorentz, polarization, decay (for 10-Me- and 10-tBu-1) and absorption (for 10-iPr- and 10-tBu-1) by ψ scans. Refinement was carried out by full-matrix least-squares measurements based on F, with weights $w = \sigma^{-2}(F_o)$. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located by different maps and refined isotropically. Crystal data, particulars of the experiments, and final R factors are given in Table II. Thermal-ellipsoid plots, tables of bond lengths and angles, torsion angles, and atom positional and thermal parameters have been deposited as supplementary material.

Results and Discussion

Computational Studies. MM2 calculations were performed for a series of 10-R anthracenones with R = H, F, Cl, Br, Me, Et, iPr, tBu, Ph, CF_3, and $SiMe_3$. The parent anthracenone is predicted to be planar in its lowest energy conformation; this agrees with recent ab initio calculations.[5] On the other hand, all of the substituted anthracenones considered are calculated to have a boat-shaped central ring with the degree of nonplanarity varying with the size of the substituent. Figure 1 presents the

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[4] Aroney, M. J.; Cleaver, G.; LeFevre, R. J. W.; Pierens, R. K. *J. Chem. Soc., B* 1971, 82.

[5] Schaefer, T.; Sebastian, R. *THEOCHEM* **1988**, *180*, 319.

[6] Destro, R.; D'Alfonso, T. B.; Simonetta, M. *Acta Crystallogr. B* **1973**, *B29*, 2214.

[7] Brown, K. L.; Fullerton, T. J. *Acta Crystallogr. B* **1980**, *B36*, 3199.

[8] Ahmed, F. R. *Acta Crystallogr. B* **1980**, *B36*, 3184.

[9] Ranwald, H. W.; Lohse, K.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1528.

[10] Roszak, A.; Engelen, B. *Acta Crystallogr. C* **1990**, *C46*, 240.

[11] Allinger, N. L. *MM2 (87)* available from QCPE, Indiana University, Bloomington, IN 47405.

[12] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[13] Stewart, J. J. P. *QCPE Program No. 455* (Version 5.0).

[14] GAUSSIAN 88. Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA.

[15] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939; Gordon, M. J.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

[16] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*: Wiley & Sons, New York, 1986.

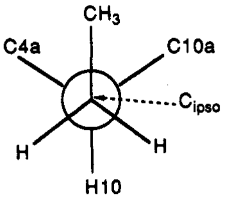
[17] Tolbert, L. M.; Khanna, R. K.; Popp, A. E.; Gelbaum, L.; Bottomley, L. A. *J. Am. Chem. Soc.* **1990**, *112*, 2373.

[18] Brisson, R. *Ann. Chim. (Paris)* **1952**, *7*, 311.

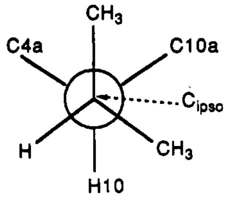
[19] Brinkmann, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Stothers, J. B.; Ternay, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 5912.

MM2 optimized structures of 10-F-1 and 10-tBu-1 as examples of the molecules in question. All the considered substituents except fluorine (see Discussion below) prefer the pseudoaxial position. This is a consequence of the nonbonding repulsive interactions of the substituent at C10 with the peri hydrogens at C4 and C5. Similar pseudoaxial preference has been recognized in 9,10-dihydroanthracenes[20a,b] and 9,10-dihydrophenanthrenes.[20c]

Substituents with sp^3-hybridized atoms attached to C10 exhibit a staggered conformation along the C10–C(Si)$_{ipso}$ bond (cf. tBu-1 in Figure 1). In 10-Et-1 the CH_3 group is located anti to H10 in the lowest energy conformation, reducing the repulsions with the peri hydrogens. For the same reason, iPr is oriented to have one methyl group anti and the other gauche to H10.



10-Et-1



10-*i*-Pr-1

The unusual pseudoequatorial preference of fluorine deserves some attention. To be sure that this prediction is not an artifact of the method used we performed some additional MO calculations by the AM1 method. This semiempirical method also predicts the planar conformer to be the global minimum for unsubstituted 1. In full accord with the MM2 results, AM1 predicts pseudoequatorial preference for fluorine and pseudoaxial preference for the other substituents considered. This verifies the MM2 results and confirms the exceptional nature of the fluorine substituent in the 9-anthracenone system.

The reason for the pseudoequatorial preference of fluorine in 10-F-1 is as follows. In this orientation, the distances between the fluorine atom and the peri H4 and H5 hydrogen atoms are equal to the sum of their van der Waals radii. This is the "ideal" nonbonding distance and results in a lowering of the total steric energy of the system. If the fluorine atom is forced to be pseudoaxial, or the anthrone moiety is forced to be planar, the F···H_{peri} distances become larger and the attractive van der Waals forces are reduced. In contrast, when more bulky substituents are forced to be pseudoequatorial, significant crowding occurs with the peri hydrogens. To avoid this unfavorable interaction, such as substituents occupy the pseudoaxial position.

Correlation of Calculated, Central-Ring Folding in 10-R-1 with the Size of the Substituent. We probed the influence of substituent size at C10 on the degree of nonplanarity of the anthracenone moiety with reference to the following variables. The value of $\Sigma\Theta$ is used as a measure of the degree of nonplanarity of the central ring. It is the sum of the absolute values of all six torsional angles defined by the carbon atoms within the ring. For a planar ring, the value of $\Sigma\Theta$ is 0; higher values of $\Sigma\Theta$ indicate, of course, a higher degree of nonplanarity. Since $\Sigma\Theta$ reflects the changes in the planarity about the entire central ring, it is a better measure of the substituent effect than is any single torsional angle or the angle between the planes defined by the outer benzene rings.

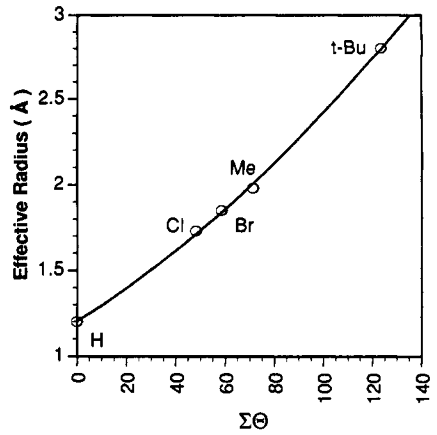


Figure 2. Plot of the calculated $\Sigma\Theta$ against the effective radius of R in some 10-R-9-anthracenones.

The size of a substituent may be assessed in various ways. The first choice would be to use the values of the van der Waals radii derived by Bondi[21] from crystallographic data. These data, however, do not include values for some of the present groups, particularly the tBu group. Since tBu is the most bulky substituent in the series, it is important to include it in the correlation. Once the smallest (H) and the bulkiest (tBu) substituents are included, the effective radii of other groups can be estimated by interpolation rather than extrapolation, a more reliable procedure.

Methods for the estimation of group size include effective radii deduced from either the geometrical features of atoms and groups (e.g., Charton's set[22]) or from certain physical processes (e.g., Sternhell's set[23]). Unfortunately, the effective radius for the tBu group is reported[23] with a large margin of error (3.6 ± 0.5 Å), and so Charton's effective radii remain as the only reasonable alternative. Charton reports 2.4 and 3.2 Å as the minimum and maximum effective radii for the tBu group.[22] According to the minimal steric interaction principle, the steric effect exerted by any group of atoms will be as small as possible. In the simplest case this means that the steric effect of a certain group may be described by its minimum size.[22] In 10-substituted 1, however, the substituents interact with two peri hydrogen atoms and so a minimization of the repulsion of the tBu group with one of the peri hydrogens leads to an increase with the other. Thus, the effective radius of this group is in our opinion larger than the minimum radius, and the same applies to the other groups with local C_3 symmetry. For this reason we employ the mean values of Charton's minimum and maximum radii for Me and tBu instead of r_{min}, in the hope that is a more reliable description of the steric requirements in question. Also, since the relative changes rather than absolute values of the effective radii are of interest, the choice of the starting value of the radii for Me and tBu is not very important.

For the first correlation we chose R = H, Cl, Br, Me, and tBu since, in addition to the reasons indicated above, they exhibit a high degree of spherical symmetry. A plot of the MM2 calculated $\Sigma\Theta$ values against the Charton's effective radii is depicted in Figure 2; there is a very good correlation between the size of the substituent at C10 and the degree

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(20) For the recent reviews see: (a) Rabideau, P. W. In *The Conformational Analysis of Cyclohexenes, Cyclohexadienes and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH; New York, 1989; Chapter 4. (b) Lipkowitz, K. B. *Ibid.* Chapter 7. (c) Rabideau, P. W.; Sygula, A. *Ibid.* Chapter 3.

(21) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley: New York, 1968.

(22) Charton, M. *Top. Curr. Chem.* **1983**, *114*, 75.

(23) Bott, G.; Field, L. D.; Sternhell, S. *J. Chem. Soc.* **1980**, *102*, 5618.

Table I. Degree of Nonplanarity of 10-R-1 As Predicted by MM2 and the Effective Radii of the Substituents Considered

				effective radius (Å)		
	$\sum\Theta$ (deg)	$\alpha 1$[a] (deg)	$\alpha 2$[b] (deg)	this work	Charton[22]	Sternhell[23]
H	0.0	0.0	0.0	1.2[c]	1.2	1.2
F	75.8	20.7	12.8	*d*	1.47	1.47
Cl	48.2	13.0	8.4	1.75[c]	1.75	1.73
Br	58.5	15.8	10.1	1.85[c]	1.85	1.85
Me	71.3	19.7	11.0	1.98[c]	1.72–2.23	1.80
Et	66.5	18.3	10.4	1.94	1.76	
iPr	96.3	26.4[e]	15.4[e]	2.36	1.96	2.2
tBu	123.4	33.6	20.1	2.80[c]	2.40–3.20	3.6
CF_3	94.3	26.0	14.6	2.33	2.10–2.73	2.2
$Si(Me)_3$	100.5	27.6	16.0	2.43	2.60–3.50	2.01
Ph	39.5	11.0	5.8	1.61	1.77–3.35	1.62

[a] Torsional angle C8a–C10a–C10–C4a = C9a–C4a–C10–C10a. [b] Torsional angle C4a–C9a–C9–C8a = C10a–C8a–C9–C9a. [c] Value taken from Charton (ref 22). [d] Not estimated, see text. [e] Average value, the molecule does not possesss a plane of symmetry.

of nonplanarity in the anthrone moiety. The correlation curve in Figure 2 may be used to estimate the effective radii of the other substituents considered. These estimates are presented in Table I together with some MM2 calculated results in Charton's and Sternhell's effective radii for comparison.

The effective radii in Table I derived from the correlation in Figure 2 show a reasonable similarity to the values obtained earlier. In general, our values of the effective radii based on MM2 calculations fall between the minimum and maximum radius values of Charton[22] which may support the validity of the approximations applied. The only exceptions are Et and iPr for which our radii are higher than the Charton values and Ph with an effective radius was found to be slightly lower than the minimum Charton value. Since the radii reported by Charton for Et and iPr are apparently minimum values, the difference is a simple consequence of using the average Charton values for Me and tBu (see above). On the other hand our estimation of the effective radii for iPr and Ph are very close to the ones reported by Sternhell (Table I). It should be noted, however, that the effective radii are expected to change with the moethod of evaluation since they characterize a given substituent in a particular physical or chemical process. Thus, the similarity of a given set of effective radii to other sets is not a necessary condition for acceptance.

The only drastic difference is found for fluorine. On the basis of the correlation shown in Figure 2 and the MM2 value of $\Sigma\Theta = 75.8°$ for 10-F-1 (Table I), a value of 2.07 Å could be assigned for the effective radius of fluorine, and this is much higher than the generally accepted value of 1.47 Å. This discrepancy, however, can be easily explained by the exceptional pseudoequatorial preference of fluorine as discussed above. The curve in Figure 2 represents the effect of the steric repulsions of pseudoaxial substituents at C10 with the peri hydrogen atoms. Since the fluorine is located in the pseudoequatorial position and is attractive rather than repulsive with respect to the peri hydrogens, it cannot fit into the correlation.

The aim of the attempted correlation was to probe the influence of the size of the substituent at C10 on the nonplanarity of the anthracenone moiety. Since, at the level of the MM2 method, there exists a good correlation of the two variables, the bulkiness of the substituent is indeed expected to play a major role in the folding of the entire molecule. Thus, if the size of the substituent decreases so does the degree of nonplanarity and a question arises as to whether the anthracenone moiety approaches planarity when the substituent size gets close to the hydrogen atom. The correlation presented in Figure 2 cannot be used for this purpose since the parent 1 was included in it. However, if unsubstituted 1 is excluded from the correlation and the remaining points (i.e., Cl, Br, Me, and tBu) are used for the same type of curve fitting, the extrapolation gives a value of 1.4 Å at $\Sigma\Theta = 0°$. This suggests that the anthracenone moiety may approach planarity even with a substituent slightly bigger than hydrogen provided that the peri repulsions are the governing factor.

So according to our calculations, planar anthracenone is the most stable conformation for isolated 1, and all distortions from planarity of the known derivatives are caused by steric interactions of the substituents and/or by intermolecular interactions in condensed phases. This conclusion is in accord with recent ab initio calculations.[5] Schaefer and Sebastian showed that at the STO-3G and 4-31G level of approximation the planar conformer of anthrone is most stable.[5] However, since the potential energy surface near the minimum is extremely flat, and, moreover, some geometrical constraints are used in the calculations for the nonplanar forms (planarity of the benzene rings[5]), we decided to repeat some of the ab initio calculations. Thus, we reoptimized the geometry of planar 1 with C_{2v} symmetry constraints at the 3-21G level and characterized the resulting structure ($E = -607.465512$ au) by calculating the vibrational frequencies at the same level of approximation. The calculations gave all positive frequencies showing that the planar conformer of 1 is a true potential energy minimum at this level of theory. The very low calculated frequency of the butterfly vibration of the molecule (39 cm^{-1}) demonstrates, however, the shallowness of the potential energy surface around the minimum in accord with the previous results of Schaefer and Sebastian.[5]

Crystal Structure Studies. To verify the theoretical studies, we determined the X-ray crystal structures of several 10-substituted anthracenones. A literature search provided only one crystal structure of interest: 10-Br-1.[6] Thus, crystal structure determinations were performed for four additional 10-R-1's where R = Me, iPr, tBu, and Ph. The crystal structure data for these derivatives are collected in Table II with some selected structural parameters presented in Table III.

Generally, there is a close correlation of the structures found in the solid state with the MM2 results obtained for the isolated molecules. All of these 10-monosubstituted 9-anthracenones exhibit nonplanarity of the central ring, which forms a boat or pseudoboat, with the substituent at C10 located in a pseudoaxial position. This is, of course, consistent with the predictions by MM2. The degree of nonplanarity is largest for 10-tBu-1 and smallest for 10-Ph-1 (Table III), again in agreement with the theoretical predictions. Also the prefered conformations of the substituents predicted by MM2 (e.g., the staggered conformations of Me, iPr, and tBu and the conformational preference of the iPr group discussed earlier) are favored as well in the solid state.

Closer comparison of the degree of folding of 10-R-1 in the solid state (Table III) with the values calculated for the isolated molecules (Table I) shows an excellent correlation for 10-Br-, 10-iPr-, and 10-tBu-1. For example the differences in the theoretical and experimental values of $\Sigma\Theta$ are 1.3° for 10-Br, 0.6° for 10-iPr, and 1.2 and 4.4° for 10-tBu (there are two symmetrically independent molecules of 10-tBu-1 in the unit cell; see Table II). Keeping in mind that $\Sigma\Theta$ is a sum of six torsional angles, the differences between the calculated and experimental values are indeed negligible. Other structural parameters describing the folding of these molecules in the crystal are

Table II. Crystal Data for the 10-R-9-Anthracenones

	R = Me	R = iPr	R = tBu	R = Ph
mol formula	$C_{15}H_{12}O$	$C_{17}H_{16}O$	$C_{18}H_{18}O$	$C_{20}H_{14}O$
mol weight	208.3	236.3	250.3	270.3
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
cell constants				
a, Å	6.1608 (5)	9.9488 (9)	19.165 (2)	9.1664 (4)
b, Å	12.5966 (13)	12.4588 (15)	8.5890 (6)	5.8995 (2)
c, Å	14.0558 (13)	11.1701 (12)	19.166 (2)	26.2821 (14)
β, deg		107.299 (7)	116.62 (1)	94.107 (4)
Z	4	4	8	4
no. of variables	194	228	488	247
D_{calc}, g cm^{-3}	1.266	1.187	1.179	1.267
radiation	Cu	Cu	Cu	Mo
temp, K	296	296	289	296
θ range, deg	2–75	2–75	2–75	1–27.5
max decay corr	1.245		1.171	
min transmission, %		92.8	96.5	
unique data	2246	2709	5792	3240
observed data $I > 3\sigma(I)$	1868	2264	4631	1871
R	0.031	0.048	0.044	0.038
R_w	0.036	0.063	0.059	0.043

Table III. Selected Structural Parameters Describing the Folding of the Central Ring of 10-R-9-Anthracenones As Determined by X-ray

	R = Me	R = iPr	R = tBu	R = Ph	R = Br[a]
$\sum\theta$	21.9	96.9	124.6[b]	16.6	59.8
			119.0		
α_1[c]	4.6	27.7	34.2	3.9	15.9
	−6.3	−25.1	−32.8	−0.3	−16.7
			35.7		
			−33.3		
α_2[d]	3.0	17.5	19.9	4.5	10.4
	−4.7	−15.0	−17.8	−0.9	−11.1
			18.6		
			−16.7		

[a] Reference 6. [b] There are two symmetry-independent molecules of 10-tBu-1 in the crystal unit cell. [c] Torsional angles C8a–C10a–C10–C4a and C9a–C4a–C10–C10a. [d] Torsional angles C4a–C9a–C9–C8a and C10a–C8a–C9–C9a.

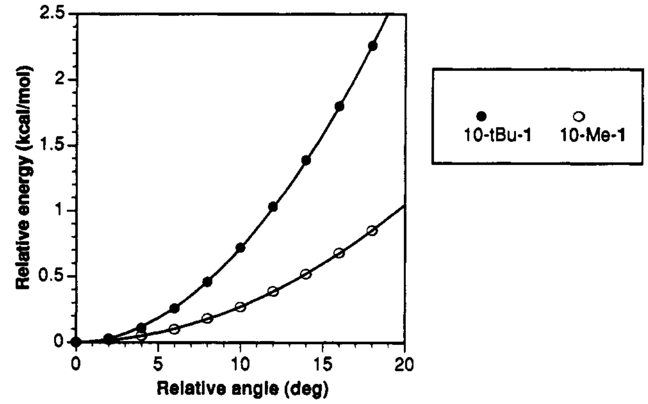

Figure 3. MM2 calculated steric energy penalty for flattening the $\alpha_1 = -\alpha_2$ torsional angle in 10-Me-1 and 10-tBu-1.

also in a very good agreement with the MM2 data.

On the other hand there is a significant disagreement between the experimental degree of nonplanarity (Table III) and the MM2 predictions for 10-Me and 10-Ph-1. The molecules in the solid state are significantly less folded than predicted for the isolated molecules. However, since MM2 works well for 10-iPr and 10-tBu-1 using the same set of parameters, it is not clear why it would fail for the other derivatives, especially the Me case. Hence, we believe that crystal packing forces may be responsible for the discrepancy.

The anthracenones with smaller substituents at C10 are expected to be more sensitive to the effects of the crystal field. Figure 3 shows the MM2 calculated relative increase in steric energy of 10-Me and 10-tBu-1 caused by a flattening of the C9a–C4a–C10–C10a and C8a–C10a–C10–C4a torsional angles from their minimum energy values. It can be seen from Figure 3 that flattening of the central ring causes a more severe energy penalty in 10-tBu-1 than in 10-Me-1. Since the lowest energy conformation of 10-R-1 is a compromise of the steric repulsions caused by the substituent and the increase in energy caused by distortion of the anthracenone moiety from planarity, the derivatives with more bulky substituents are expected to be "stiffer" than the ones with smaller groups at C10. This may explain, in part, the discrepancies between the theoretical and crystal structure data for small substituents. However, since there is no discrepancy between the MM2 prediction and the crystal structure results for 10-Br-1, which has a substituent similar in size to Me, we feel that specific crystal structure packing requirements are responsible for the disagreement between the calculated and experimental results for 10-Me-1 and 10-Ph-1.

According to the theoretical results, the anthracenone moiety approaches planarity as the size of the substituent approaches that of the hydrogen atom. Since the crystal structure studies show that the MM2 method generally gives a good prediction of the structure of 9-anthracenones, and since in the solid the derivatives with small substituents at C10 are even less puckered than calculated, it must be expected that the parent 1 is planar in the crystal. Earlier molecular mechanics calculations[24] suggest that crystal packing forces slightly flatten the nonplanar ring in the structurally related 9,10-dihydroanthracene (**2**) as compared to the isolated molecule. The results herein show a similar effect for 10-Me-1 and 10-Ph-1. Hence, we conclude that 1 is planar and that the observed large independent out-of-plane vibration of the oxygen atom in the crystal[1,2] may be attributed to the shallowness of the potential energy surface.[5]

The conformational properties of 9-anthracenones are quite different from those of the structurally related 9,10-dihydroanthracenes.[20a,b] The parent 9,10-dihydroanthracene (**2**) is significantly nonplanar both in the crystal[25] and in the gas phase.[26] Apparently, in going from

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(24) Sygula, A.; Holak, T. *Tetrahedron Lett.* **1983**, *24*, 2893.

(25) (a) Ferrier, W. G.; Iball, J. *Chem. Ind. (London)* **1954**, 1296. (b) Herbstein, F. H.; Kapon, M.; Reisner, G. M. *Acta Crystallogr. B* **1986**, *42*, 181.

2 to 1, the introduction of the additional sp^2-hybridized center (C9) conjugated with the benzene rings is sufficient for planarization of the molecule. Although the potential energy surface for 2 is also flat in the vicinity of the minimum,[20a,b,27] the size of the substituent in 9-monosubstituted 2′'s does not significantly influence the degree of nonplanarity of the system. For example, crystal structure determination gives the value of the angle between the planes of the benzene rings to be 145° for unsubstituted 2[25] and 147° for 9-tBu-2.[28] Similarly molecular mechanics calculations[20b] predict the angle in question to be 148° and 143° for 9-Me-2 and 9-tBu-2, respectively, again suggesting only slight changes in the degree of nonplanarity with drastic changes in substituent size. A plausible explanation for the difference in behavior of 9,10-dihydroanthracenes as compared to 9-anthracenones is as follows: If a substituent is attached to significantly nonplanar 2 in the pseudoaxial orientation at C9, it is located relatively far away from the peri hydrogen atoms at C1 and C8 despite its size. Thus, at this distance, the substituents avoid significant van der Waals overlap and there is little repulsion to distort the original geometry. This is in contrast to the 9-anthracenones wherein the central ring would like to be planar.

Conclusions

The MM2 results for a series of 10-monosubstituted 9-anthracenones show a very significant correlation between the degree of nonplanarity of the central ring and the size of the substituent. An extrapolation of this dependency suggests that the anthracenone moiety approaches planarity as the effective size of the substituent approaches the size of a hydrogen atom. This supports a planar structure for the minimum energy conformation of the parent 1 in the gas phase. Ab initio calculations with geometry optimization using the 3-21G basis set were performed for planar 1 and the resulting structure was characterized by calculation of vibrational frequencies, indicating that the planar structure is a true minimum on the potential energy surface at this level of theory.

Crystal structure determinations of several 10-R-9-1's show the central ring to form a boat or pseudoboat in each case considered with the substituent located in the pseudoaxial position in accord with the MM2 results. The degree of planarity of the substituted anthracenones in the solid state correlates well with the MM2 predictions for R = iPr, tBu, and Br. On the other hand, the 10-Me-1 and 10-Ph-1 are found to be significantly less puckered in the crystal than predicted by MM2 for the isolated molecules. This discrepancy is attributed to the crystal packing forces.

The generally good correlation of the MM2 results with the X-ray data provides strong support for the validity of the calculations in predicting optimum structures for anthracenones. Since MM2 as well as ab initio calculations predict anthracenone itself to be planar in its lowest energy conformation, and since crystal packing forces are found to flatten some of the derivatives of 1 as compared to the isolated molecules, we expect 1 to be planar in the solid state. The observed, large independent out-of-plane vibration of the oxygen atom in the crystal of 1[1,2] is attributed to the shallowness of its potential energy surface.[5]

Comparison of the 9-anthracenone system with the structurally related 9,10-dihydroanthracene reveals significant differences in the response of the two systems to the size of substituents at C10 or C9, respectively. The latter system is virtually insensitive to the size of the substituent in sharp contrast to the former. This difference is attributed to the differences in the preferred conformations of the unsubstituted compounds, 1 and 2.

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Supplementary Material Available: Thermal-ellipsoid plots and tables of bond lengths and angles, torsion angles, and atom positional and thermal parameters for 10-Me, 10-iPr, 10-tBu, and 10-Ph-1 (33 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(26) Shin, Y.-D.; Saigusa, H.; Zgierski, M. Z.; Zerbetto, F.; Lim, E. C. *J. Chem. Phys.* **1991**, *94*, 3511.

(27) The very recent determination of the gas-phase barrier for inversion in 2 gives the value of 1.9 kcal/mol only.[26]

(28) Brennan, T.; Puttkey, E. F.; Sundaralingam, M. *J. Chem. Soc. D* **1971**, 1490.