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Substituent Effects on the Photoisomerization of Anthracenes to Their 9,10-Dewar Isomers

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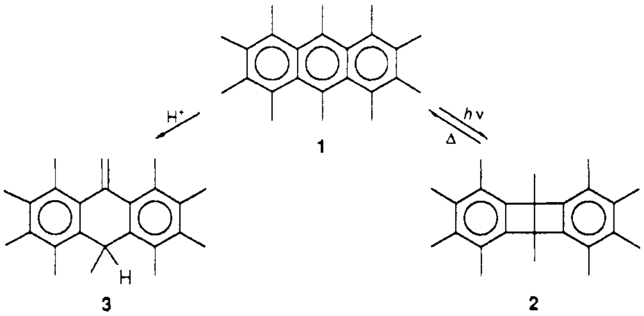
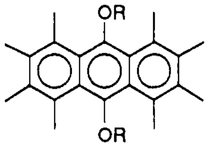
Irradiation of 9,10-dialkoxyoctamethylanthracenes **4–6** and of 9-methoxyoctamethylanthracene **11** at −78 °C in toluene-d_8 gave the corresponding 9,10-Dewar isomers. All Dewar isomers were thermally less stable than decamethyl(9,10-Dewar anthracene) and reverted to the corresponding anthracenes at temperatures from −30 to −60 °C. Under similar irradiation conditions, 1,2,3,4,5,6,7,8-octamethylanthracene (**12**) gave a free radical, possibly **17**, which reverted to **12** above −30 °C. 1,8,9,10- and 1,5,9,10-Tetramethylanthracenes (**13** and **14**) were particularly sensitive to photooxidation, whereas 1,4,9-trimethylanthracene (**15**) gave photodimers. Decamethyl- and 9,10-dimethoxyoctamethylphenanthrenes were photochemically inert. Improved syntheses of **12** and **15** are described.

Although Dewar benzene,[1] Dewar naphthalene,[2] and substituted analogues have been extensively studied, there are relatively few examples of Dewar anthracenes[3-7] or the Dewar isomers of higher fused ring aromatics. Relief of steric strain is a factor in the two known photoisomerizations of anthracenes to 9,10-Dewar isomers.[5,7,8] For example, decamethylanthracene (**1**) has multiple peri interactions[9] that may be relieved by photoisomerization of **2**. However, the strain in **1** can also be relieved by its irreversible and facile acid-catalyzed isomerization to **3**, in which the central ring is nonaromatic. Although **2** could be isolated as a white solid at room temperature, it reverted to **1** on warming in benzene, indicating that, despite the peri interactions, **1** is thermodynamically more stable than **2**. Similar results were obtained later with 9-*tert*-butylanthracene and its Dewar isomer.[7]



The photoisomerization of **1** to **2** is clean, as is the thermal isomerization of **2** to **1**, suggesting possible utility in an energy-storage device. However, the sensitivity of **1** to traces of acid gradually results in the buildup of **3**. Consequently we decided to study the 9,10-bisalkoxy analogues **4–6** where the irreversible isomerization should be blocked. It was hoped that by varying the size of R the interconversion of the anthracenes and their Dewar isomers might be controlled. In this paper we describe the preparation and irradiation of **4–6**, as well as a number of related analogues.



4: R = Me
5: R = Et
6: R = iPr

Results and Discussion

Synthesis of Starting Materials. 9,10-Dimethoxyoctamethylanthracene (**4**) was described earlier,[10] prepared from **7** (R = Me) via the sequence shown. We synthesized

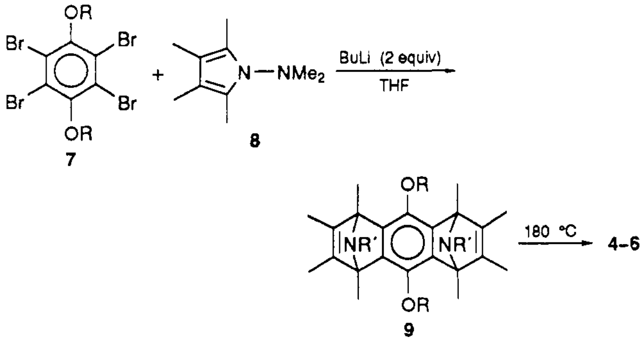


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Table I. ^{1}H NMR Spectral Data of Anthracenes and Dewar Anthracenes

anthracene	δ	Dewar anthracene	δ
4	2.38 (s, 12 H) 2.76 (s, 12 H) 3.33 (s, 6 H)	D4	1.88 (s, 12 H) 2.28 (s, 12 H) 3.71 (s, 6 H)
5	1.26 (t, J = 7 Hz, 6 H) 2.32 (s, 12 H) 3.07 (s, 12 H) 3.48 (q, J = 7 Hz, 4 H)	D5	1.37 (t, J = 7 Hz, 6 H) 1.89 (s, 12 H) 2.30 (s, 12 H) 4.07 (q, J = 7 Hz, 4 H)
6	1.08 (d, J = 6 H, 12 H) 2.47 (s, 12 H) 3.19 (s, 12 H) 4.12 (sept, J = 6 Hz, 2 H)	D6	1.57 (d, J = 6 Hz, 12 H) 1.83 (s, 12 H) 2.31 (s, 12 H) 4.62 (sept, J = 6 Hz, 2 H)
11	2.33 (s, 6 H) 2.36 (s, 6 H) 2.72 (s, 6 H) 3.04 (s, 6 H) 3.40 (s, 3 H) 8.58 (s, 1 H)	D11	1.90 (s, 6 H) 1.93 (s, 6 H) 2.13 (s, 6 H 2.35 (s, 6 H) 3.46 (s, 6 H) 4.95 (s, 1 H)

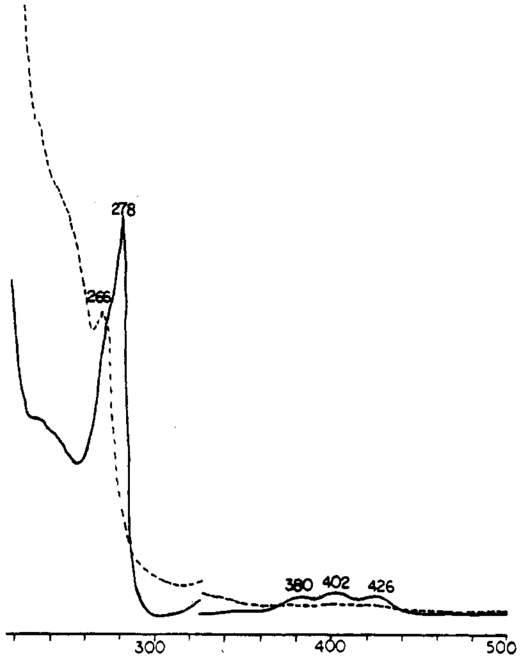
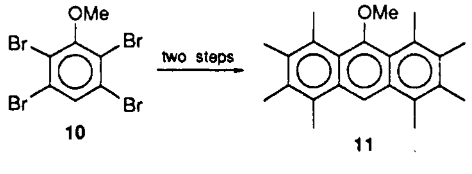
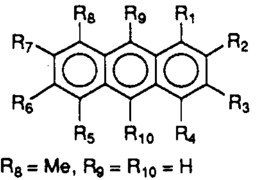


Figure 1. UV spectra of 5 (solid line) and D5 (broken line) in hexane at −45 °C.

5 and 6 via the same route, in 50–60% overall yield. The monomethoxy analogue 11 was similarly prepared from 10.

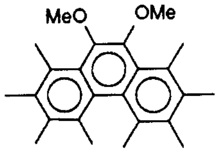


In addition, we prepared and irradiated several polymethylanthracenes less substituted than 1. These included 12–15, prepared by using previously developed methodology.



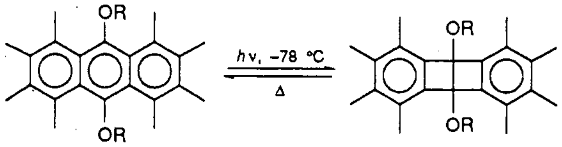
12: R_1–R_8 = Me, R_9 = R_{10} = H
13: R_1 = R_8 = R_9 = R_{10} = Me, R_2–R_7 = H
14: R_1 = R_5 = R_9 = R_{10} = Me, remaining R's = H
15: R_1 = R_4 = R_9 = Me, remaining R's = H

Finally, for comparison with the anthracenes, we prepared phenanthrene 16, using the same method described earlier for decamethylphenanthrene.[11]



16

Photochemical Results. The Methoxyanthracenes. Solutions of anthracenes 4–6 in benzene-d_6 (approximately 5×10^{-2} M) were irradiated at room temperature in an NMR tube (Hanovia 450 W, Pyrex, 60–90 min). Unlike 1, which rapidly isomerized to 2 under similar conditions, no reaction occurred with 4–6 as judged by the constancy of the NMR spectrum. However, when the irradiations were repeated at −78 °C in toluene-d_8, the desired Dewar anthracenes were cleanly formed, as indicated by the NMR spectra listed in Table I. Similar results were obtained with 11.



D4: R = Me
D5: R = Et
D6: R = iPr

The structures of the Dewar anthracenes were clear from their spectra and from their facile thermal reversion to the corresponding anthracenes. Some generalizations can be made regarding the proton spectra. In 4–6, the OCH protons experience a 0.4–0.6-ppm downfield shift on going from the anthracene to the Dewar form. This is presumably due to deshielding of each OR group by the other as the two groups are brought closer when the C9–C10 bond is formed. This explanation is supported by the fact that no such change in the methoxyl protons occurs when 11 is converted to D11, because 11 has a hydrogen in place of the alkoxy group at C10. On the other hand, the aromatic proton in 11 (δ 8.58) is shifted upfield to δ 4.95 in D11, as C10 becomes tertiary and aliphatic. Also, a substantial upfield shift of all aromatic methyl signals (approximately 0.5–0.7 ppm) is observed on going from the anthracenes to the Dewar isomers (where the aromatic rings are benzenoid).

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(11) Hart, H.; Shamouilian, S. *J. Org. Chem.* 1981, *46*, 4874–4876.

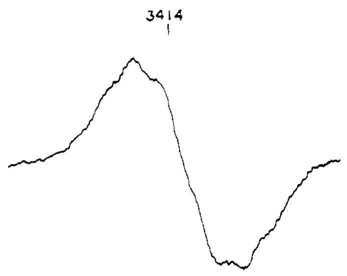
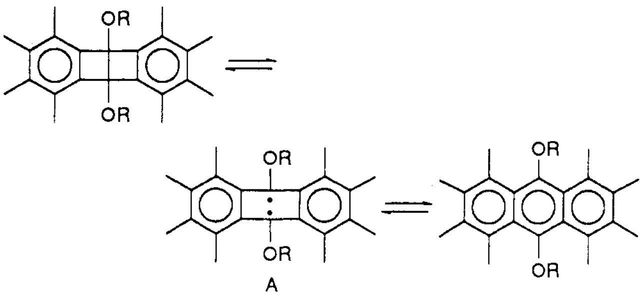


Figure 2. ESR spectrum of the radical obtained on irradiation of 12 in toluene at −100 °C.

The ^{13}C spectra of **D4** and **D11** were also instructive; they showed seven and 13 signals, respectively, as required by the symmetry. The "cyclobutane" carbons appeared at δ 54.84 in **D4** and as two peaks at δ 54.57 and 54.63 in **D11**. Other features of the spectra were consistent with the structures (see Experimental Section).

The ultraviolet spectra of **D4**, **D5**, and **D11** were obtained by carrying out the photolyses in a quartz UV cell in hexane at −45 °C. The Dewar anthracenes all showed a λ_{max} at 266–272 nm, in contrast with their anthracene precursors, which showed typical long-wavelength absorptions above 400 nm (see Figure 1).

The alkoxy-substituted Dewar anthracenes prepared here were thermally much less stable than **2**. They could not be readily isolated since they reverted to the anthracenes above −30 °C. This stability difference compared with **2** can be rationalized if the thermal isomerization proceeds via a diradical intermediate A, since alkoxy groups should be better than methyl groups at stabilizing radical centers. Diradical intermediates have been generally implicated in Dewar arene thermal isomerizations.[1,2,4,6,7]



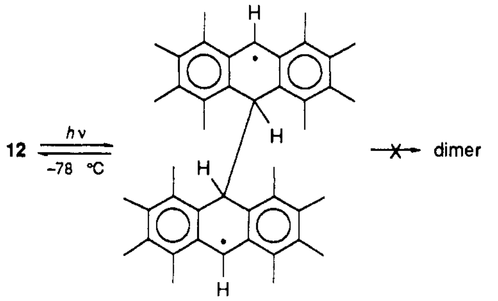
A

The thermal stability also seemed to *decrease* with increasing bulk of the OR group. Approximate half-lives were 1 h at −30 °C for **D4**, 30 min at −50 °C for **D5**, and even less for **D6**, which could not be kept for any appreciable time above −60 °C. Apparently torsional strain in the Dewar structure increases as the size of the OR group increases. Also, the number of unhindered conformations decreases as R increases in bulk, resulting in an entropic destabilization of the Dewar form.

Even though it has one less methoxyl substituent, **D11** had approximately the same half-life as **D4**. Perhaps one less peri substituent (i.e., less steric strain in the anthracene) balances the effect of one less oxygen stabilizing the diradical intermediate.

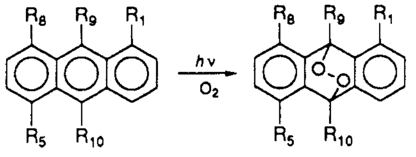
Photochemical Results. The Methylanthracenes. Irradiation of 1,2,3,4,5,6,7,8-octamethylanthracene (**12**) proceeded in a curious way, quite different from that of its decamethyl analogue **1**. Brief irradiation of toluene solutions of **12** at −78 °C (either degassed or not) resulted in the complete disappearance of the ^1H NMR spectrum; a radical was produced, as evidenced by an ESR spectrum (Figure 2). The radical signal decayed at temperatures above −30 °C, and **12** was recovered quantitatively. As far as we know, there is no precedent in the literature for this type of photochemical behavior of an anthracene.

Because of lack of detail in the ESR spectrum, we can only speculate as to the nature of the radical species. One likely possibility is the diradical **17**.[12] Diradicals of this type have been discussed previously as possible intermediates in anthracene photodimerizations.[13] In the present instance, if **17** is formed, it may be too sterically hindered to cyclize to the usual type of anthracene photodimer. Instead, it simply dissociates on warming to give back the monomer **12**. On the other hand, crowded anthracenes with 9,10-substituents, such as **1** or **4–6**, do not form analogues of **17** presumably because of steric hindrance around the ethane-like C–C bond; instead they photoisomerize unimolecularly to Dewar anthracenes.



17

In view of radical formation of **12**, it was of interest to irradiate several somewhat less methylated analogues. Neither **13** nor **14** gave a Dewar isomer (irradiation at −78 °C) nor did they produce photodimers or radicals. They were exceptionally sensitive to photooxidation, however, and they had to be prepared and isolated in the dark since even laboratory fluorescent lights were sufficient to bring about their conversion to **18** and **19**, respectively.



13, 14

18: $R_1 = R_8 = R_9 = R_{10} = Me$, $R_5 = H$
19: $R_1 = R_5 = R_9 = R_{10} = Me$, $R_8 = H$

Finally, removal of one of the 9,10-methyl substituents permitted photodimerization. The example studied was 1,4,9-trimethylanthracene (**15**), which gave two photodimers (not separated), thought to be the head-to-tail dimers **20** (major) and **21** (minor); see the Experimental Section for the NMR descriptions.

Irradiation of Phenanthrenes. Unlike the anthracenes, neither decamethylphenanthrene[11] nor its 9,10-dimethoxy analogue **16** gave any photoproducts under similar irradiation conditions. The starting materials were recovered quantitatively.

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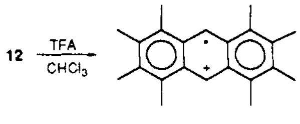
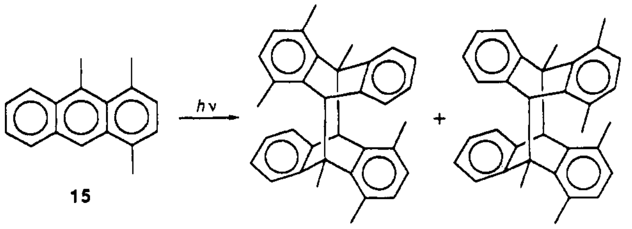
(12) Oligomers of 17 are also a possibility. The radical concentration is not known, and even small amounts may suffice to prevent observation of an NMR spectrum. A different radical species, with a different ESR spectrum, is obtained when 12 is treated with trifluoroacetic acid (TFA) in chloroform. The species in this case is stable indefinitely at room temperature, but on aqueous quench again gives back 12. This species is most likely the radical cation



(13) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum Press: New York, 1976; p 62.



15 20 21

Summary. Persubstituted anthracenes such as **1**, **4**–**6**, and even the slightly less hindered **11** photoisomerize to Dewar isomers, but 9,10-alkoxy substituents destabilize the Dewar isomers with respect to thermal reversion to the starting anthracenes. Octamethylanthracene **12** gives a radical on irradiation, possibly **17**; the radical is reconverted to **12** above −30 °C. Tetramethylanthracenes **13** and **14** do not photoisomerize or dimerize, but are exceptionally sensitive to photooxidation. Trimethylanthracene **15** forms photodimers, and persubstituted phenanthrenes (i.e., **16**) are photochemically inert.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on either a Bruker WM 250-MHz or a Varian T-60 spectrometer using $(CH_3)_4Si$ as the internal standard. ESR spectra were measured on a Varian E-4 EPR spectrometer. IR spectra were recorded on a Perkin-Elmer Model 167 spectrometer. Mass spectra were measured at 70 eV by Ernest Oliver, using a Finnigan 4000 spectrometer with the INCOS data system. UV spectra were recorded on a Varian Carey 219 spectrometer. Melting points were determined by using a Mel-Temp apparatus and are uncorrected. The drying agent throughout was anhydrous magnesium sulfate, and chromatography was done with 230–400-mesh silica gel. Analyses were performed by either Spang Microanalytical Laboratory, Eagle Harbor, MI, or Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada.

2,3,5,6-Tetrabromo-1,4-diethoxybenzene (7, R = Et). Ethyl bromide (5 mL) was added at once to a solution of tetrabromohydroquinone[14] (10.65 g, 25 mmol) and potassium hydroxide (2.8 g) in 30 mL of methanol, and the resulting solution was heated at reflux for 20 h. The solvent was removed, and the residue was taken up in ether (100 mL), washed successively with 0.5 N sodium hydroxide, 0.1 N hydrochloric acid, and brine, and dried. Removal of the ether left a tan solid, which was recrystallized from methanol to give 7.2 g (60%) of **7** (R = Et) as white needles: mp 150–151 °C; ^1H NMR ($CDCl_3$) δ 1.45 (t, *J* = 6 Hz, 6 H), 4.00 (q, *J* = 6 Hz, 4 H); mass spectrum, *m/e* (relative intensity) 482 (13), 454 (7), 426 (100), 131 (87).

2,3,5,6-Tetrabromo-1,4-diisopropoxybenzene (7, R = iPr). According to a similar procedure as for **7** (R = Et), a solution of tetrabromohydroquinone (21.3 g, 50 mmol), potassium hydroxide (5.61 g, 0.1 mol), and isopropyl iodide (20.4 g, 0.12 mol) in 75 mL of methanol was heated at reflux for 40 h. Workup as above gave a dark brown solid, which was eluted through 8 cm of Florisil with 1:1 chloroform–hexanes. The resulting orange solid was recrystallized from methanol to give 10.4 g (41%) of **7** (R = iPr) as pale yellow needles: mp 104–105 °C; ^1H NMR ($CDCl_3$) δ 1.40 (d, *J* = 6 Hz, 12 H), 4.75 (sept, *J* = 6 Hz, 2 H); mass spectrum, *m/e* 510 (M^+), 43 (base peak).

9,10-Diethoxy-1,2,3,4,5,6,7,8-octamethylanthracene (5). To a solution of **7** (R = Et) (2.4 g, 5 mmol) and 2 g of *N*-(*N*,*N*-dimethylamino)-2,3,4,5-tetramethylpyrrole (**8**)[10] in 50 mL of tetrahydrofuran under argon at −78 °C was added *n*-butyllithium (12 mmol in 25 mL of hexane) dropwise over 2 h. The mixture was allowed to come slowly to room temperature. Methanol (1 mL) was added, followed by water (50 mL). The product was extracted into methylene chloride, washed with water, and dried and the solvent removed. The resulting waxy yellow solid (**9**, R = Et) was heated under vacuum at 180 °C for 30 min. The black residue was eluted through 8 cm of Florisil with 1:1 chloroform–hexane and recrystallized from methanol–water to give 0.95 g (50%) of **5** as bright yellow needles: mp 171–172 °C; ^1H NMR (toluene-d_8) δ 1.26 (t, *J* = 7 Hz, 6 H), 2.32 (s, 12 H), 3.07 (s, 12 H), 3.48 (q, *J* = 7 Hz, 4 H); mass spectrum, *m/e* (relative intensity) 378 (33), 349 (60), 321 (100), 305 (10), 290 (10), 235 (9), 161 (12). Anal. Calcd for $C_{26}H_{34}O_2$: C, 82.46; H, 9.05. Found: C, 82.45; H, 9.09.

9,10-Diisopropoxy-1,2,3,4,5,6,7,8-octamethylanthracene (6). The procedure was similar to that for **5**, but 2.55 g (5 mmol) of **7** (R = iPr) and 2 g of **8** were used. The crude product was recrystallized from acetone to give 1.2 g (60%) of **6** as small yellow crystals: mp 218–219 °C; ^1H NMR (toluene-d_8) δ 1.08 (d, *J* = 6 Hz, 12 H), 2.47 (s, 12 H), 3.19 (s, 12 H), 4.12 (sept, *J* = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.1, 21.0, 22.0, 75.4, 127.7, 127.9, 133.6, 151.4; mass spectrum, *m/e* (relative intensity) 406 (8), 363 (5), 321 (100), 305 (7), 43 (50). Anal. Calcd for $C_{28}H_{38}O_2$: C, 82.71; H, 9.42. Found: C, 82.76; H, 9.46.

2,3,5,6-Tetrabromo-4-(bromomethyl)anisole (22). A solution of 4-methoxy-2,3,5,6-tetrabromotoluene[10] (21.9 g, 0.05 mol) and bromine (16 g, 0.1 mol) in CCl_4 (1000 mL) at reflux was irradiated with a high-intensity lamp for 3 h. The solution was allowed to cool, washed with dilute sodium bisulfite, and dried and the solvent removed. Recrystallization of the off-white residue from ethanol gave 25.6 g (99%) of **22** as white needles: mp 162–164 °C; ^1H NMR ($CDCl_3$) δ 3.8 (s, 3 H), 4.8 (s, 2 H); mass spectrum, *m/e* (relative intensity) 514 (1), 436 (65), 315 (21), 234 (30), 153 (40), 85 (37), 74 (100).

2,3,5,6-Tetrabromo-4-(acetoxymethyl)anisole (23). A solution of **22** (20.4 g, 0.04 mol) in acetic anhydride (150 mL) containing 2 g of potassium acetate was heated at reflux for 3 h, cooled, and poured into an ice–sodium hydroxide (2 N) mixture. The resulting light brown precipitate was filtered, dissolved in methylene chloride (100 mL), washed successively with dilute sodium bicarbonate and water, and dried. Removal of the solvent left a sandy solid, which was recrystallized from methanol to give 19.7 g (99%) of **23** as white needles: mp 124–125 °C; ^1H NMR ($CDCl_3$) δ 2.1 (s, 3 H), 3.85 (s, 3 H), 5.55 (s, 2 H); mass spectrum, *m/e* (relative intensity) no M^+, 437 (1), 415 (1), 375 (7), 357 (1), 74 (5), 43 (100).

2,3,5,6-Tetrabromo-4-(hydroxymethyl)anisole (24). To a solution of **23** (20 g, 0.04 mol) in ethanol (150 mL) was added 200 mL of 1 N potassium hydroxide, and the mixture was heated at reflux for 4 h and then cooled in an ice bath. The white crystals were collected by vacuum filtration and recrystallized from acetone to give 16.7 g (92%) of **24** as white needles: mp 172–173 °C; ^1H NMR ($CDCl_3$) δ 2.2 (br s, 1 H), 3.8 (s, 3 H), 5.15 (s, 2 H); mass spectrum, *m/e* (relative intensity) 454 (56), 373 (44), 330 (38), 266 (100), 223 (34), 141 (32), 74 (29).

2,3,5,6-Tetrabromoanisole (10). A solution of tetra-*n*-butylammonium permanganate[15] (4.80 g, 13 mmol) in 50 mL of pyridine under argon was added to a solution of **24** (4.54 g, 10 mmol) in 50 mL of pyridine at room temperature, and the resulting purple solution was heated at 40–50 °C for 6 h (solution turned brown). The mixture was cooled to room temperature and poured into dilute hydrochloric acid containing sodium bisulfite. The white precipitate that formed was filtered and recrystallized from methanol to give 2.9 g (70%) of **10** as small white needles, mp 122–124 °C (lit.[16] mp 120.5 °C).

9-Methoxy-1,2,3,4,5,6,7,8-octamethylanthracene (11). The procedure was similar to that for **5**, using 2.17 g (5 mmol) of **10** and 2 g of **8**. The crude product was eluted through 10 cm of silica gel with 10:1 hexane–chloroform and then recrystallized from acetone–ether to give 0.2 g (20%) of **11** as bright yellow needles: mp 234–235 °C; ^1H NMR (toluene-d_8) δ 2.33 (s, 6 H), 2.36 (s, 6 H), 2.72 (s, 6 H), 3.04 (s, 6 H), 3.40 (s, 3 H), 8.58 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.92, 17.57, 17.73, 19.33, 62.22, 114.36, 124.57, 127.72, 128.11, 131.17, 132.11, 133.78, 155.36; mass spectrum, *m/e* (relative intensity) 320 (80), 305 (100), 41 (100). Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 86.17; H, 8.66.

1,2,3,4,5,6,7,8-Octamethylanthracene (12). A solution of *n*-butyllithium (22 mmol) in hexane (50 mL) was added dropwise over 3 h to 1,2,4,5-tetrabromobenzene[17] (3.9 g, 10 mmol) and

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tetramethylfuran (3 g) dissolved in 50 mL of dry toluene under argon at −78 °C. The mixture was allowed to warm slowly to room temperature, and 1 mL of methanol was added. The mixture was washed with water and dried and the solvent removed. The resulting waxy solid was recrystallized from methanol to give 2.0 g (71%) of the diadduct 1,2,3,4,5,6,7,8-octamethyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-diepoxide (**25**) as pale yellow crystals: mp 290–296 °C; ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 12 H), 1.78 (s, 12 H), 6.82 (s, 2 H); mass spectrum, *m*/*e* (relative intensity) 322 (14), 268 (2), 236 (10), 225 (100).

To a suspension of 1 mL of titanium tetrachloride in 50 mL of dry tetrahydrofuran (THF) under argon at 0 °C was added 1.4 g of zinc powder. The steel gray suspension was heated to reflux, and a solution of diepoxide **25** (0.32 g, 1 mmol) in 50 mL of THF with added dropwise (15 min). The mixture was heated at reflux (8 h), cooled to room temperature, and poured into dilute hydrochloric acid. The resulting purple mixture was extracted with methylene chloride, the organic layer was washed with water and dried, and the solvent was removed. The crude product was recrystallized from chloroform–hexane to give 0.25 g (80%) of **12** as small yellow crystals: mp 292–294 °C (lit.[18] mp 298–300 °C); ^{1}H NMR (toluene-d_8) δ 2.30 (s, 12 H), 2.71 (s, 12 H), 8.83 (s, 2 H); mass spectrum, *m*/*e* (relative intensity) 290 (100), 275 (9).

1,5,9,10-Tetramethylanthracene (14) and 1,8,9,10-Tetramethylanthracene (13). To a solution of tetrabromo-*p*-xylene[10] (8.44 g, 20 mmol) and 2-methylfuran (4.1 g, 50 mmol) in 200 mL of dry toluene under argon at −23 °C was added *n*-butyllithium (45 mmol in 100 mL of hexane) dropwise over 3 h. The mixture was allowed to warm slowly to room temperature and was stirred overnight. Methanol (1 mL) was added, the mixture was washed with water and dried, and the solvent was removed. The yellow waxy solid that remained was recrystallized from methanol (the mother liquors were saved) to give 1.8 g (34%) of 1,5,9,10-tetramethyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-diepoxide (**26**) as off-white crystals: mp 248–252 °C; ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 6 H), 2.25 (s, 6 H), 5.50 (d, *J* = 2 Hz, 2 H), 6.85 (br s, 2 H), 6.95 (br d, *J* = 2 Hz, 2 H); mass spectrum, *m*/*e* (relative intensity) 266 (25), 240 (12), 223 (43), 197 (100), 181 (69), 165 (43), 152 (23), 43 (95).

The mother liquor from the above recrystallization was evaporated to give a yellow oil, which was crystallized from hexane to give 1.5 g (28%) of a 3:2 mixture of *syn*- and *anti*-1,8,9,10-tetramethyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-diepoxide (**27**): mp 174–180 °C; ^{1}H NMR ($CDCl_3$) (major isomer) δ 2.10 (s, 6 H), 2.30 (s, 3 H), 2.38 (s, 3 H), 5.65 (m, 2 H), 6.8–7.1 (m, 4 H), (minor isomer) δ 2.10 (s, 6 H), 2.40 (s, 3 H), 2.45 (s, 3 H), 5.65 (m, 2 H), 6.8–7.1 (m, 4 H); mass spectrum (mixture), *m*/*e* (relative intensity) 266 (19), 240 (13), 223 (23), 197 (46), 181 (37), 165 (27), 152 (15), 85 (26), 43 (100).

Deoxygenation of **26** was carried out as for **25** except that the reaction mixture was worked up in the dark. The crude product was recrystallized from methanol to give 0.20 g (85%) of **14** as yellow needles: mp 71–72 °C; ^{1}H NMR (toluene-d_8) δ 2.65 (s, 6 H), 2.87 (s, 6 H), 7.14–7.24 (m, 4 H), 8.01 (d, *J* = 9 Hz, 2 H); mass spectrum, *m*/*e* (relative intensity) 234 (100), 219 (62), 202 (16), 108 (28). Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.17; H, 7.84.

Deoxygenation of **27** carried out as for **26** gave a yellow oil, which was crystallized from methanol–ether to give 135 mg (57%) of **13**[19] as yellow flakes: mp 80–82 °C; ^{1}H NMR (toluene-d_8) δ 2.66 (s, 6 H), 2.71 (s, 3 H), 2.79 (s, 3 H), 7.16–7.25 (m, 4 H), 8.02 (d, 2 H); mass spectrum, *m*/*e* (relative intensity) 234 (97), 219 (100), 202 (29), 189 (14), 101 (29), 94 (16).

1,4,9-Trimethylanthracene (15).[20] This compound was prepared by following the same procedure as for 1,4,5,8,9-pentamethylanthracene[21] but using benzenediazonium carboxylate hydrochloride in place of its 3,6-dimethyl analogues.[22] The product was recrystallized from methanol: mp 80–81 °C (lit.[20] mp 81 °C); ^{1}H NMR ($CDCl_3$) δ 2.63 (s, 3 H), 2.85 (s, 3 H), 3.15 (s, 3 H), 6.97 (s, 2 H), 7.20–8.15 (m, 4 H), 8.20 (s, 1 H).

4,5-Dibromo-3,6-diiodoveratrole (28). A solution of 4,5-dibromoveratrole[23] (18 g, 0.061 mol) and mercuric oxide (42 g) in 160 mL of trifluoroacetic acid was heated at reflux for 4 h and then cooled in an ice bath. The resulting white solid (4,5-dibromo-3,6-bis(trifluoroacetatomercurio)veratrole) was filtered and heated at 70–75 °C for 8 h with iodine (60 g) and potassium iodide (40 g) in 200 mL of water (mechanical stirring). The mixture was cooled, and the resulting solid was taken up in chloroform, washed successively with 10% sodium thiosulfate, dilute sodium bicarbonate, and water, and dried. Solvent removal and recrystallization of the off-white residue from chloroform–methanol gave 26.4 g (79%) of **28** as white needles: mp 144–145 °C; mass spectrum, *m*/*e* (relative intensity) 532 (25), 504 (21), 489 (14), 405 (5), 390 (15), 254 (13), 203 (53), 155 (61), 127 (100), 104 (42), 76 (54).

9,10-Dimethoxy-1,2,3,4,5,6,7,8-octamethyl-1,4,5,8-tetrahydrophenanthrene 1,4:5,8-Diendoxide (29). To a solution of **28** (1.37 g, 2.5 mmol) and tetramethylfuran (1 g, 8 mmol) in 50 mL of dry ether at −78 °C was added *n*-BuLi (9 mmol in 50 mL of hexane) dropwise over 4 h. The mixture was allowed to warm to room temperature and was stirred overnight. Methanol (1 mL) was added, the mixture was washed with water and dried, and the solvent was removed. A light yellow oil of crude **29** remained: ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 6 H), 1.80 (s, 6 H), 1.85 (s, 6 H), 1.86 (s, 6 H), 3.75 (s, 6 H); mass spectrum, *m*/*e* (relative intensity) 382 (10), 339 (100), 328 (29), 296 (86), 285 (50), 281 (79), 165 (45), 123 (87), 71 (89).

9,10-Dimethoxy-1,2,3,4,5,6,7,8-octamethylphenanthrene (16). To a suspension of titanium tetrachloride (1 mL) in 50 mL of dry THF under argon at 0 °C was added 1.4 g of zinc powder. The steel-gray suspension was heated to reflux, and a solution of the crude diendoxide **29** (above) in 50 mL of THF was added dropwise (15 min). The mixture was heated at reflux for 8 h, then cooled to room temperature, and poured into dilute hydrochloric acid. The organic product was extracted with methylene chloride, washed with water, and dried. The crude product was recrystallized from methanol to give 0.22 g (25% from **25**) of **16** as light yellow needles: mp 187–188 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.36 (s, 6 H), 2.41 (s, 6 H), 2.80 (s, 6 H), 3.86 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 16.78, 16.98, 18.05, 20.82, 60.10, 118.50, 127.20, 131.31, 131.94, 134.08, 146.20; mass spectrum, *m*/*e* (relative intensity) 350 (53), 307 (100), 292 (16), 277 (12), 175 (16), 160 (18), 131 (19). Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.62. Found: C, 82.12; H, 8.75.

General Photolysis Procedure. The arene to be photolyzed (10–12 mg) was dissolved in 0.5 mL of benzene-d_6, placed in a 5-mm NMR tube, and flushed with nitrogen. The tube was taped to the water-cooled jacket of a Hanovia 450-W medium-pressure lamp and irradiated for 60–90 min at room temperature. Runs at −78 °C were conducted similarly, except that the solvent was toluene-d_8, the lamp and cooling jacket with the sample taped to it were immersed in a dry ice–isopropyl alcohol bath, and dry nitrogen was passed through the cooling jacket.

After irradiation, the sample tube was immediately transferred to the Bruker WM 250 NMR spectrometer, preset at a suitable temperature between −60 °C and room temperature, and the spectrum was recorded. Results are given in Table I (for protons) and elsewhere in the text. Half-lives given in the text for the

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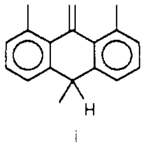
i

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Dewar anthracenes were determined by following changes in their ^{1}H NMR spectra with time.

^{13}C NMR Spectra. **For D4**: δ 15.64, 15.87, 54.84, 101.27, 129.65, 135.12, 144.05. **For D11**: δ 15.34, 15.52, 15.61, 15.96, 54.57, 54.63, 99.53, 129.70, 133.64, 134.38, 136.93, 143.99, 144.05. These spectra were measured at −60 °C. **D5** and **D6** were too short-lived to obtain ^{13}C spectra.

UV Spectra. The spectrum of **D5** in Figure 1 was obtained by irradiating a solution of **5** in hexane in a quartz Dewar-UV cell at −45 °C; the spectrum was recorded at that temperature. In a similar manner, λ_{max} for **D4** was at 270 nm, and for **D11** at 272 nm. **D6** was too unstable at −45 °C to obtain a UV spectrum.

Endoperoxides 18 and 19. Brief irradiation (30 min) of an undegassed solution of **13** in benzene-d_6 in an NMR tube as described in the general photolysis procedure gave endoperoxide **18**: ^{1}H NMR (C_6D_6) δ 1.79 (s, 3 H), 1.99 (s, 3 H), 2.07 (s, 6 H), 6.71–7.06 (m, 6 H); mass spectrum, *m/e* (relative intensity) 266 (4), 251 (9), 234 (100), 219 (36), 85 (20). In a similar manner, irradiation of **14** gave endoperoxide **19**: ^{1}H NMR (C_6D_6) δ 1.96 (s, 6 H), 2.09 (s, 6 H), 6.75–7.01 (m, 6 H); ^{13}C NMR (C_6D_6) δ 18.56, 21.87, 81.24, 119.66, 126.91, 131.53, 131.88, 143.80 (one peak under the solvent peak); mass spectrum, *m/e* (relative intensity) 266 (4), 234 (100), 219 (32), 85 (22), 40 (16).

Irradiation of 1,4,9-Trimethylanthracene (15). Samples of **15** were irradiated in several solvents (benzene-d_6, pyridine-d_5, and chloroform-*d*) according to the general photolysis procedure. The singlet at δ 8.20 (aromatic proton at C10) in the spectrum of **15** disappeared, and new singlets appeared at δ 4.27 and 4.45 (in $CDCl_3$), area ratio 5:1, ascribed to the bridgehead protons in **20** and **21**, respectively. In addition, the major product **20** showed three methyl singlets approximately 0.5 ppm upfield from those in **15** (in $CDCl_3$, at δ 2.25, 2.39, and 2.55) whereas the minor isomer **21** showed a singlet at δ 2.50 (ratio of δ 2.39/2.50 = 5:1; the other methyl peaks for **21** were coincidental with those of **20** at δ 2.25 and 2.55; in pyridine-d_5, two of the three methyl signals for **21** were nicely resolved). The photoproducts were stable even after 3 h at 60 °C.

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Abnormally High IR Frequencies for the Carbonyl Group of Semicarbazones of the Benzaldehyde and Acetophenone Series

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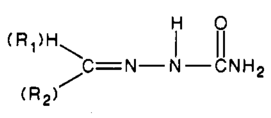
We have synthesized 86 semicarbazones of variously substituted benzaldehyde and acetophenone and of several other aldehydes and ketones for comparison. The IR data in Nujol mull revealed numerous abnormally high frequencies for the carbonyl of semicarbazones of up to ca. 1760 cm^{-1} (cf. 1690 cm^{-1} as a normal value for semicarbazones carbonyls and 1640–1650 cm^{-1} for the amide and urea carbonyls). These high C=O frequencies shift to normal values in DMSO solution. The origin of the high C=O frequencies could not be ascribed to the stereoelectronic effects of the substituents on the aromatic ring. It appeared that the high C=O frequencies are caused by the solid-state structure. The X-ray structural determination of two semicarbazones indicated a network of H-bonds in which each C=O is involved in a bifurcated H-bond with NH_2 and NH from two different molecules. The solution and solid-state ^{13}C NMR studies of semicarbazones are also described.

Introduction

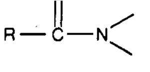
Semicarbazones I are very common derivatives of aldehydes and ketones and are frequently used in the qualitative organic analysis of these carbonyl compounds.[1,2]



$$(R_1)H(R_2)C{=}N{-}NH{-}C(=O)NH_2$$

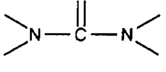
semicarbazones I

The IR frequencies of the carbonyl group of the semicarbazones drew interest rather early. Wang[3] observed that the IR frequency of the carbonyls of the semicarbazones is normally found at ca. 1690 cm^{-1} (in KBr), which appeared abnormally high as compared to those of amides II and ureas III at 1640–1650 cm^{-1}.



$$R{-}C(=O){-}N<$$

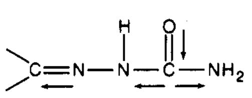
amides II



$$>N{-}C(=O){-}N<$$

ureas III

Wang attempted to explain the shift to higher frequencies of I vs III by the inductive effect of the extra nitrogen in I: The combined inductive effects would pull



$$>C{=}N{-}NH{-}C(=O){-}NH_2$$

the π cloud of carbonyl closer to the carbon, diminishing the polar character of the C=O. This would cause a rise in the IR frequency of the C=O.

We were astonished to find during a routine organic qualitative analysis laboratory experiment that *o*-nitrobenzaldehyde semicarbazone exhibits an abnormally high C=O frequency at 1737 cm^{-1} (in Nujol mull). A literature search revealed that some isolated cases of the abnormally high C=O frequencies of semicarbazones were observed earlier. Thus, Davison and Christie[4] report 1745 cm^{-1} for

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