Photochemical Hydrogen Migration in Methylanthronylidenes

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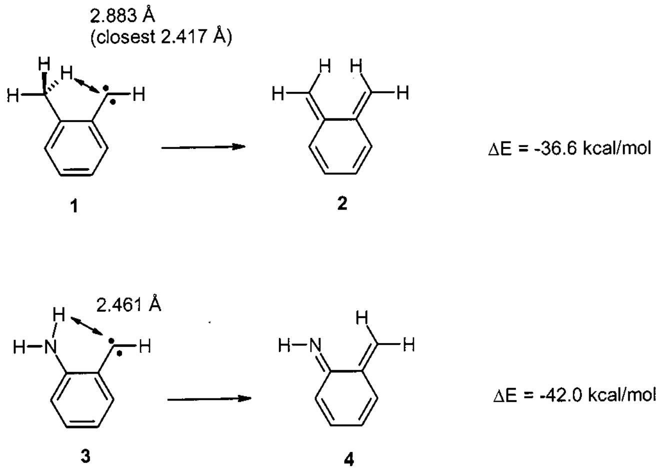
The photochemistry of 4-methyl-9,10-diazoanthrone (**7a**) and 1,4-dimethyl-9,10-diazoanthrone (**7b**) was investigated in argon matrices at 10 K. Visible-light irradiation results in the formation of the anthronylidenes **5a** and **b**, respectively, which were identified by oxygen trapping, by comparison of the IR and UV/Vis spectra with that of the parent anthronylidene **6**, and by comparison of the IR spectrum with that calculated by DFT methods. The carbenes **5** are thermally stable under the conditions of matrix isolation; however, irradiation with visible or UV light results in the rearrangement to the quinone methides **10a** and **b**.

Introduction

Hydrogen migrations are among the most important carbene reactions and in many cases limit carbene life times.[1−6] The rearrangement of matrix-isolated *o*-tolylcarbene (**1**) to give *o*-xylylene (**2**) occurs at temperatures as low as 4.6 K and was thoroughly investigated by Chapman and McMahon (Scheme 1).[7] The small temperature dependence of the rate of rearrangement and the large kinetic isotope effect observed suggests a tunneling mechanism for this hydrogen migration.

Irradiation of *o*-aminophenyldiazomethane in argon at 10 K did not lead to *o*-aminophenylcarbene (**3**) but rather directly to *o*-iminoquinone methide (**4**).[8] It is not clear whether the hydrogen shift in this system is a thermal reaction of carbene **3** with a very small activation barrier or occurs via excited states of either **3** or its diazo precursor.

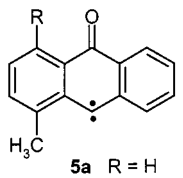
Here we describe the photochemical hydrogen shifts in anthronylidenes **5a** and **5b** which are related to carbenes **1** and **3** with respect to the arrangement of the carbene center and the γ-hydrogen atom. The photoproducts were identified as quinone methides with extended π systems.



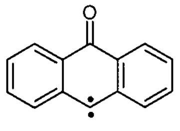
Scheme 1. Rearrangements of carbenes **1**[7] and **3**[8] to give the corresponding quinone methides **2** and **4**, respectively; the reaction energies were calculated at the UB3LYP/6−31G(d,p) level for the triplet carbenes **1** and **3** and at the B3LYP/6−31G(d,p) level of theory for the quinone methides **2** and **4**

Results and Discussion

Irradiation of 4-methyl-9,10-diazoanthrone (**7a**), matrix-isolated in argon at 10 K, with visible light ($\lambda > 420$ nm) results in the rapid decrease of the characteristic IR absorptions of diazo compound **7a** at 2047 (ν_{NN}) and 1656 cm^{-1} (ν_{CO}) and formation of 4-methylanthronylidene (**5a**) with the most intense IR bands at 1622, 1581, and 1285 cm^{-1}. As expected, the IR spectrum of **5a** is very similar to that of the parent anthronylidene **6**, which exhibits the corresponding absorptions at 1626 (s), 1580 (vs, $\nu_{C=O}$), and 1292 (s) cm^{-1}.[9] Further evidence for the identity of **5a** comes from the comparison of the experimental IR spectrum with vibrational data calculated for triplet **5a** at the UB3LYP/6−31G(d,p) level of theory (Figure 1, Table 1). The calculations very nicely reproduce the experimental spectrum. In the UV/Vis spectrum a band with λ_{max} = 350 nm and a broad absorption with a maximum around 420 nm is assigned to carbene **5a**. This visible absorption causes the ma-



5a R = H
5b R = CH_3



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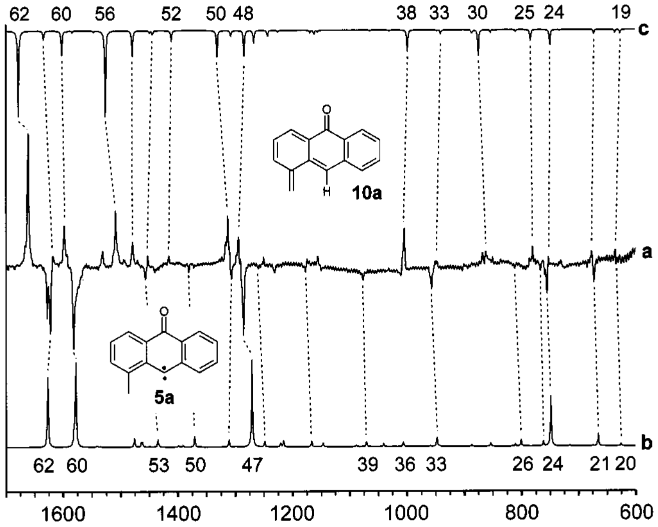


Figure 1. (a) Difference IR spectrum in absorbance showing the rearrangement **5a** → **10a** on 420-nm irradiation; bands pointing downwards disappear during the irradiation and are assigned to **5a**, bands pointing upwards are assigned to the newly formed **10a**; (b) IR spectrum of **5a** calculated at the B3LYP/6−31G(d,p) level of theory; (c) IR spectrum of **10a** calculated at the B3LYP/6−31G(d,p) level of theory

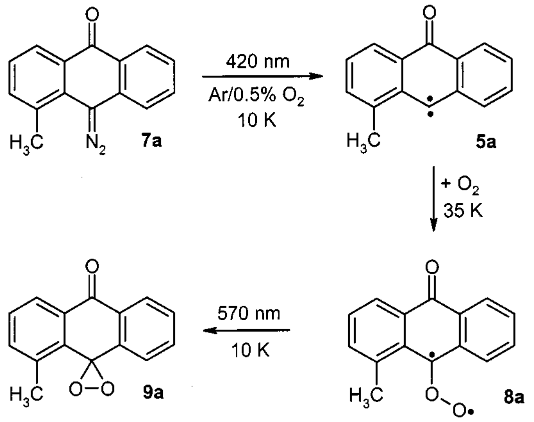
Table 1. Experimental and calculated [B3LYP/6−31G(d,p)] IR-spectroscopic data of 4-methylanthronylidene (**5a**)

$\tilde{\nu}_{exp}$ [cm^{-1}][a]	$I_{rel,\ exp}$[b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,\ calcd.}$[b]	No.
634.2	7	626	2	20
673.4	15	666	14	21
755.2	36	749	57	24
767.1	6	762	6	25
812.5	3	801	8	26
957.4	27	948	10	33
1010.4	18	1007	4	36
1077.1	18	1071	5	39
1231	7	1249	6	46
1285.2	59	1271	100	47
1306.4	26	1311	8	49
1381	18	1371	12	50
1440.2	8	1435	9	53
1581.4	100	1578	95	60
1622.3	67	1627	80	62
1627.7	19			

[a] Argon, 10 K. − [b] Relative intensity based on the strongest peak. − [c] B3LYP/6−31G(d,p); the assignment of calculated to experimental vibrations is based on band positions and relative intensities and only tentative.

trix to turn yellow during irradiation of the diazo precursor.

On annealing in a 0.5% O_2-doped argon matrix at 35 K, carbene **5a** reacts with O_2 to give carbonyl oxide **8a**, which on subsequent 570-nm irradiation rearranges to dioxirane **9a**. The rapid reaction with molecular oxygen is a further indication for the triplet ground state of **5a**.Carbonyl oxide **8a** is an intense red compound and in the IR exhibits a strong absorption at 961 cm^{-1} assigned to the O−O stretching vibration. The IR spectra of **8a** and **9a** are very similar to that of the parent anthraquinone *O*-oxide and the corresponding dioxirane, respectively.[9] This sequence, carbene−carbonyl oxide−dioxirane, is highly characteristic of carbenes[10][11] and has been frequently used to identify matrix-isolated oxocyclohexadienylidenes.[12][13]



In contrast to carbene **1**, which rapidly rearranges at cryogenic temperatures,[7] and **3**, which could not even be generated under the conditions of matrix isolation,[8] carbene **5a** is stable in an argon matrix at temperatures up to 35 K (at higher temperatures the matrix rapidly evaporates). Several hours of irradiation with λ > 420 nm, or several minutes with λ > 350 nm, is required to induce the hydrogen migration. During this irradiation of **5a** the color of the matrix changes from yellow to purple, and in the visible region of the spectrum a very broad absorption extending from 420 to 620 nm is growing in (Figure 2). The purple photoproduct was assigned the structure of 5-methylene-5*H*-anthracene-1-one (**10a**) by comparison of the experimental and calculated [B3LYP/6−31G(d,p)] IR spectrum. Characteristic vibrations in the spectrum of **10a** are the carbonyl stretching vibration at 1661 cm^{-1} and the C=C stretching vibration of the methylene group at 1617 cm^{-1}. In *o*-benzoquinone methide these absorptions are found at 1657 and 1604 cm^{-1}, respectively.[14]

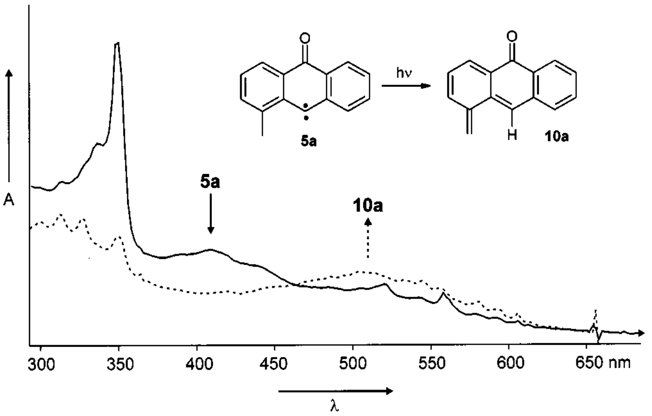


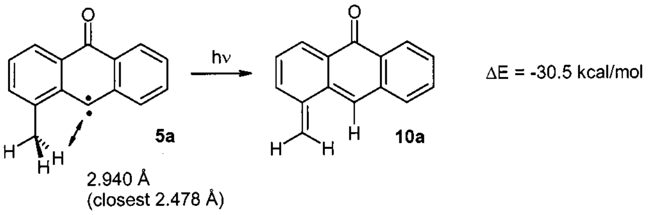
Figure 2. UV/Vis spectra showing the rearrangement **5a** → **10a** on 420-nm irradiation.; solid line: spectrum obtained after several min 420-nm irradiation, bands assigned to carbene **5a**; dotted line: after several hours irradiation the carbene is almost completely transformed to **10a**

According to the DFT calculations this rearrangement is exothermic by 30.5 kcal/mol. The distance of the migrating hydrogen atom to the carbene center is calculated to be 2.94

Table 2. Experimental and calculated [B3LYP/6−31G(d,p)] IR-spectroscopic data of 5-methylene-5*H*-anthracene-1-one (**10a**)

$\tilde{\nu}_{exp}$ [cm^{-1}][a]	$I_{rel, exp}$[b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel, calcd.}$[b]	No.
1661.0	100	1678	100	62
1617.5	27	1634	11	61
1598	56	1602	29	60
1559.3	5	1584	2	58
1531.6	8	1547	2	57
1508.6	64	1526	100	56
1479	13	1479	30	55
1452.1	2	1449	3	54
		1444	5	53
1415.8	2	1411	13	52
1312.9	51	1331	31	50
1294	35	1284	30	48
1269.7	1	1267	15	47
1250.7	19	1243	7	46
1155.9	20	1162	5	43
1004.9	39	999	25	38
950.8	12	941	5	33
899.9	2	887	4	32
886.2	1	886	2	31
852.5	13	875	30	30
857.4	2	854	3	29
850.8	5	847	1	28
780.7	23	784	13	25
753.3	19	750	18	24
731.4	6	733	1	23
677.1	20	673	5	21
635.5	7	636	4	20
628.6	2	627	5	19
537.5	5	541	9	17
517.2	10	512	16	15

[a] Argon, 10 K. – [b] Relative intensity based on the strongest peak. – [c] B3LYP/6−31G(d,p); the assignment of calculated to experimental vibrations is based on band positions and relative intensities and is only tentative.



Scheme 2. Rearrangement of anthronylidene **5a** to quinone methide **10a**; the reaction energy was calculated at the UB3LYP/6−31G(d,p) and B3LYP/6−31G(d,p) level of theory for triplet carbene **5a** and quinone methide **10a**, respectively

Å in the minimum conformation and 2.478 Å if the methyl group is rotated to the closest distance of the hydrogen atom and carbene center (Scheme 2, Figure 3). Since the methyl group can easily rotate even in solid argon, the latter distance is more important for the discussion of the hydrogen abstraction by the carbene center. To compare the conditions of the **5a** → **10a** rearrangement with that of the **1** → **2** and **3** → **4** rearrangement, we calculated the reaction energies of these reactions to 36.6 and 42.0 kcal/mol, respectively (Scheme 1). Although the energies of the triplet species **1** and **3** were calculated with unrestricted and that of the singlet species **2** and **4** with restricted wavefunctions, the systematic error using different methods should be similar for all three rearrangements, and thus the calculated trends in the energies of rearrangement should be reliable.

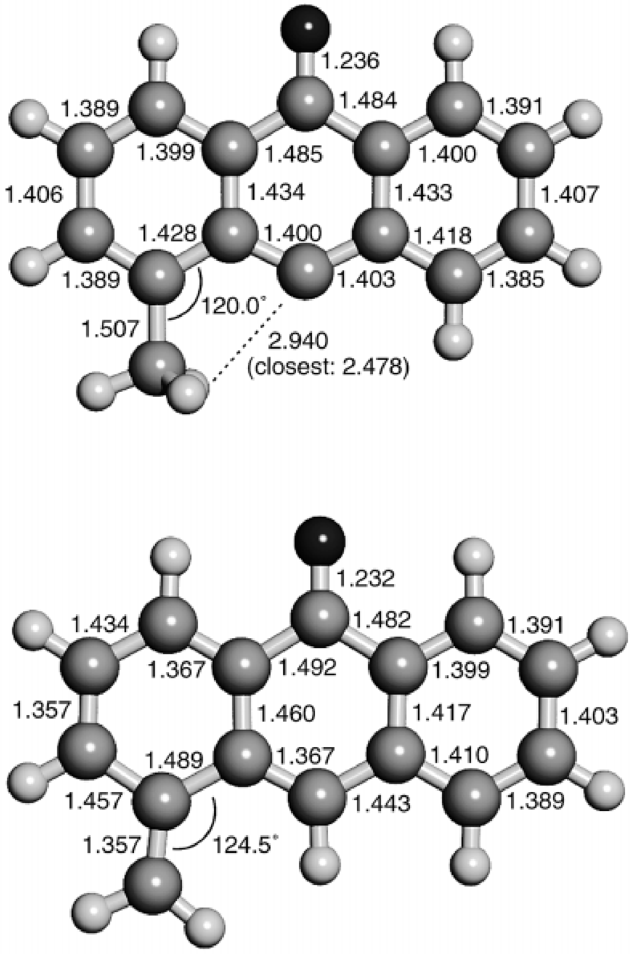
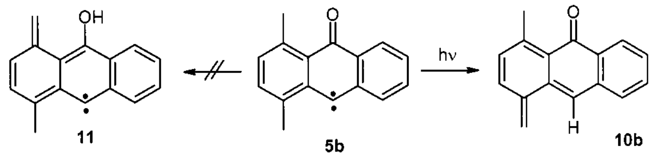


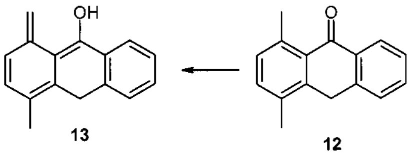
Figure 3. Some geometric data of **5a** (top) and **10a** (bottom) calculated at the B3LYP/6−31G(d,p) level of theory

Irradiation (λ > 420 nm) of matrix-isolated 1,4-dimethyl-9,10-diazoanthrone (**7b**) at 10 K produced 1,4-dimethylanthronylidene (**5b**) in high yield, which was identified by comparison of the IR spectrum with that of **5a** and **6**. In contrast to carbene **5a**, there are now two possible pathways for the hydrogen transfer in **5b**: Migration of a hydrogen atom from the 1-methyl group to the carbene center should lead to quinone methide **10b**, in analogy to the photochemistry of **5a**; migration of a hydrogen atom from the 4-methyl group to the carbonyl oxygen atom (photoenolization) would result in the formation of carbene **11**. Photoenolizations are common for 1,4-naphthoquinones and anthraquinones bearing methyl groups in *peri* positions. Thus Wirz and co-workers investigated the photoenolization of 5-methyl-1,4-naphthoquinone, which on irradiation in ethanol at 77 K forms the blue (λ_{max} = 580 nm) photoenol 4-hydroxy-5-methylidene-1(5*H*)-naphthalenone.[15][16] At room temperature the quinone methide rapidly rearranges back to the naphthoquinone (lifetime 8 µs to 90 ms, depending on the polarity of the solvent). The corresponding enolization of 1-methylanthraquinone to 9-hydroxy-1,10-

anthraquinone-1-methide was studied by Gritsan and coworkers.[17] Grummt and Friedrich were able to characterize the initially formed diradicals by EPR spectroscopy.[18] This quinone methide is unstable in unpolar solvents even at 77 K, while in ethanol glasses no rearrangement was observed up to 120 K. To demonstrate that the photoenolisation is not limited to quinones, we investigated the photochemistry of 1,4-dimethylanthrone **12**. Indeed, irradiation with $\lambda > 350$ nm in ethanol at 77 K produced enol **13** with a very broad absorption in the visible region between 500 and 580 nm.

Irradiation of carbene **5b** gave quinone methide **10b** in a clean reaction as the only product. Both the UV/Vis and the IR spectrum are similar to those of **10a**, while other photoproducts are not observed.This clearly demonstrates that hydrogen abstraction by the carbene center is preferred compared to the photoenolization, although a considerable spin density is located at the oxygen atom and the distance the 4-methyl hydrogen atom would have to travel is comparable to that of the 1-methyl hydrogen atom. However, the formation of **10b** is estimated to be more exothermic than the formation of carbene **11**. Obviously, the reaction is governed by the higher thermodynamic stability of **10b** compared to **11**.





Conclusion

In conclusion, anthronylidenes **5** substituted with methyl groups in the carbene *peri* positions are thermally stable at cryogenic temperatures but photochemically rearrange to quinone methides **10** with extended π systems. For the carbenes **1**, **3**, and **5** the distances the hydrogen atoms have to migrate are very similar (2.41 to 2.45 Å, Schemes 1 and 2). The hydrogen migration is highly exothermic with reaction energies increasing from 30.5 (**5a** → **10a**), to 36.5 (**1** → **2**), and finally 42.0 kcal/mol for the **3** → **4** rearrangement. With 30.5 kcal/mol the **5a** → **10a** rearrangement is considerably less exothermic than the other hydrogen migrations, which is in line with the higher kinetic stability of **5a** compared to **1** and **3**. Obviously, the extended delocalization of one of the unpaired electrons in carbenes **5** results in a thermodynamic stabilization with respect to the quinone methide **10**, which in turn leads to a higher activation barrier and thus kinetic stability of carbenes **5**

Experimental Section

4-Methyl-9,10-diazoanthrone (**7a**) and 1,4-dimethyl-9,10-diazoanthrone (**7b**) were synthesized by diazo-group transfer to the corresponding anthrones.[19] − ^{1}H-NMR spectra were taken with a Bruker AM 400. − Mass spectra (EI 70 eV) were taken with a Finnigan MAT 8430. − Matrix isolation experiments were performed by standard techniques with an APD DE-204SL and an APD DE-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) on top of a CsI (IR) or sapphire (UV/Vis) window with a rate of approximately 0.15 mmol/min. To obtain optically clear matrices the spectroscopic window was retained at 30 K during deposition, and the matrix was subsequently cooled to 10 K. − IR: Bruker IFS66 FTIR spectrometer with a standard resolution of 1 or 0.5 cm^{-1} in the range 400−4000 cm^{-1}. − UV/Vis: Hewlett-Packard 8452A diode-array spectrophotometer with a resolution of 2 nm. Irradiations were carried out with use of Osram HBO 500 W/2 or Ushio USH-508SA mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water. For broad-band irradiation Schott cut-off filters were used (50% transmission at the wavelength specified). For narrow-band irradiation interference filters in combination with dichroic mirrors ("cold mirrors") were used. − The DFT calculations were carried out employing Becke's three parameter functional B3LYP[20] and Pople's 6−31G(d,p) basis set.[21] All calculations were performed with the GAUSSIAN 94[22] or GAUSSIAN 98[23] set of programs.

4-Methyl-9,10-diazoanthron (7a): IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 2047.4 (100), 1661.7 (7), 1656 (45), 1606.5 (31), 1598.3 (12), 1483.7 (30), 1426.6 (17), 1352.2 (5), 1321.7 (12), 1298.5 (6), 1291 (14), 1259.3 (12), 1187.5 (20), 1096.4 (5), 1020.3 (5), 968.6 (14), 850.1 (4), 771.3 (4), 757.4 (15), 684.6 (11), 650.2 6), 598.8 (6) cm^{-1}.

1,4-Dimethyl-9,10-diazoanthron (7b): IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 2053.7 (7), 2045.4 (100), 1650.9 (47), 1604.1 (34), 1580.6 (9), 1483.5 (35), 1447.2 (6), 1391.9 (5), 1381.7 (21), 1294.6 (30), 1278.2 (15), 1252.6 (38), 1200.6 (7), 1174.9 (9), 1071.2 (4), 1036.6 (11), 973.9 (5), 939.2 (13), 851.7 (8), 838.1 (5), 759.1 (15), 651 (6), 527.7 (5) cm^{-1}.

Anthronylidene 5b: IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 1621.4 (80), 1608.9 (30), 1578.3 (90), 1569.5 (15), 1451.9 (54), 1437.5 (21), 1382.4 (24), 1297.2 (42), 1271.8 (100), 1253.1 (24), 1180.7 (23), 1022.2 (9), 947.6 (57), 845.4 (50), 813 (25), 756.7 (23), 677 (52), 669 (12), 659 (9), 517.1 (15) cm^{-1}.

10b: IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 1648.9 (100), 1633.8 (11), 1612.5 (21), 1595.6 (60), 1573.9 (20), 1474.6 (71), 1372.2 (24), 1323 (12), 1286.9 (50), 1261.4 (34), 1218.8 (7), 1155.1 (7), 1087 (10), 1031.2 (73), 1018.2 (8), 951.5 (32), 899.8 (40), 842.2 (10), 797.4 (12), 750 (64), 671.7 (9), 661.3 (6) cm^{-1}.

Acknowledgments

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