Influence of Bridgehead Substitution and Ring Annelation on the Photophysical Properties of Polycyclic DBO-Type Azoalkanes

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The photophysical data for the polycyclic, bridgehead-substituted derivatives **1**−**10** of the photoreluctant diazabicyclo[2.2.2]oct-2-ene (DBO) are presented. Substitution on the bridgehead positions with radical-stabilizing substituents enhances the photoreactivity (Φ_r) and decreases the fluorescence quantum yields (Φ_f) and lifetimes (τ) compared to the parent DBO. The annelated rings have no influence on the photoreactivity, except when steric interactions with an α substituent hinder the optimal radical-stabilizing conformation. The fused rings and some of the bridgehead substituents reduce the solvent-induced quenching of the singlet-excited azo chromophore by steric shielding of the azo group and, thus, increase the fluorescence quantum yields and lifetimes.

Introduction

Bi- and polycyclic azoalkanes are precious precursors for highly strained molecules, e.g., homotropolidenes,[1] dewarbenzenes,[2] or bicyclo[2.2.0]hexanes,[1a,3] which are otherwise difficult to come by. These compounds result through the cyclization of the intermediary diradicals, which are generated by photochemical nitrogen loss from the azoalkane.[4] A requisite for high product yields is efficient nitrogen extrusion; unfortunately, some azoalkanes are photoreluctant to lose molecular nitrogen. A notorious example is the bicyclic 2,3-diazabiyclo[2.2.2]oct-2-ene (DBO), whose very low reaction quantum yield (0.018) impressively displays its poor photoreactivity.[5] Nevertheless, the low photoreactivity of DBO may be improved by placing radical-stabilizing groups at the bridgehead position (α to the azo chromophore),[6] by raising the temperature during the photolysis,[7] or by *exo* annelation of strained rings on the bicyclic skeleton.[8] Despite the extensive work on azoalkane chemistry in the past, little is still known on the efficiency of *endo* annelation and on radical-stabilizing substituents other than phenyl[8] and vinyl[6] in enhancing the photoreactivity of DBO. To understand mechanistically the photoreluctance of DBO and its derivatives, we have investigated herein the photophysical properties of the *endo*-annelated and bridgehead-substituted azoalkanes **1**−**10** (Chart 1). Specifically, the quantum yields of azoalkane disappearance (Φ_r) and fluorescence (Φ_f) as well as the fluorescence lifetimes (τ) of these azoalkanes have been determined. The present results demonstrate substantial electronic and particularly steric effects on the photophysical behavior of DBO-type azoalkanes.

Results and Discussion

Ester-Substituted Azoalkanes. The extensive set of photophysical data for the ester-substituted azoalkanes **1**, **2**, **3a**, **4**−**7**, and **8a** shall be discussed first because they allow for recognition of some definitive trends in the photophysical properties of these compounds (Table 1). For example, ester groups significantly promote the photoreactivity of these azoalkanes in comparison to the parent DBO (Table 1), as reflected in the quantum yields of azoalkane disappearance (Φ_r). This increase of reactivity is based on the radical-stabilizing effect of the ester group [9] on the incipient carbon-radical site in the diazenyl diradical, which enhances the nitrogen elimination. Expectedly, the higher photoreactivity of these ester-substituted azoalkanes is accompanied by a dramatic (as much as 10-fold) reduction of the fluorescence efficiency when compared to DBO (Table 1). Furthermore, it is evident that there is no significant structural influence of the *endo*-annelated rings on the photoreactivity, since all Φ_r values of the ester-substituted azoalkanes are identical ($\Phi_r = 0.38 \pm 0.05$) within the error limit (Table 1). Nevertheless, a substantial structural effect on the fluorescence properties may be noticed: Successive exchange of the cyclopropyl groups in **1** by norbornyl groups in **2** and **3a** increases significantly both the fluorescence efficiencies (Φ_f) and lifetimes (τ), with the latter especially being much higher than expected. What is responsible

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Chart 1

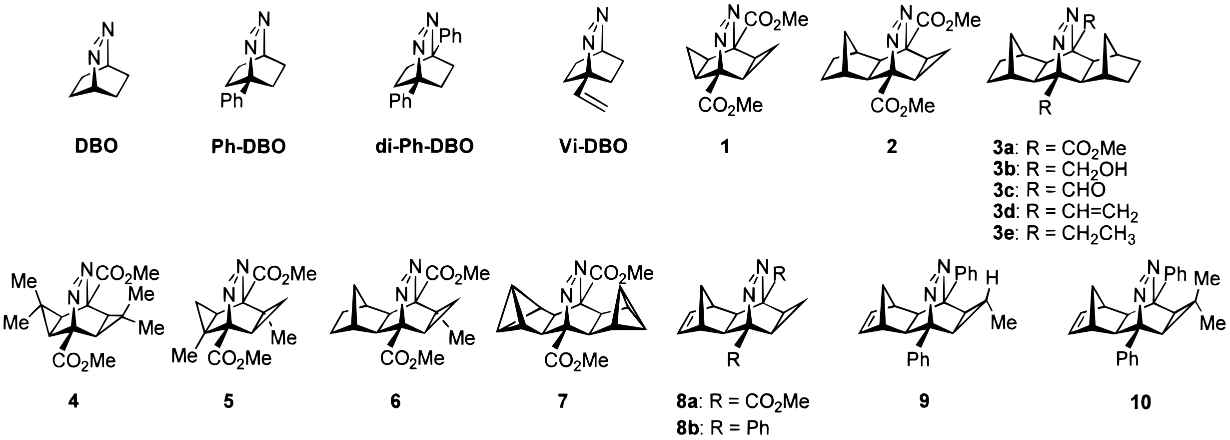

Table 1. Photophysical Data of the Polycyclic Azoalkanes 1−10 (MeCN, 20 °C)

azo-alkane	Φ_f[a]	Φ_r[b]	Φ_d[c]	τ [ns][d]	$10^5 k_f$ [s^{-1}][e]	$10^5 k_r$ [s^{-1}][f]	$10^5 k_d$ [s^{-1}][g]
DBO[h]	0.39	0.018	0.59	434	9.0	0.41	14
Ph-DBO[h]	0.0014	1.0	0	2.5	5.6	4000	0
Vi-DBO[h]	0.0009	1.0	0	0.56	5.3	18000	0
1	0.0066	0.40	0.59	9.2	7.2	435	641
2	0.041	0.36	0.60	139	2.9	26	43
3a	0.090	0.35	0.56	273	3.3	13	21
3c	0.049	0.64	0.31	111	4.4	58	28
3d	0.16	0.67	0.17	268	5.9	25	6.3
3e	0.19	0.0090	0.80	263	7.1	34	30
4	0.041	0.33	0.63	101	4.1	33	62
5	0.0024	0.33	0.67	9.5	2.5	347	705
6	0.043	0.42	0.54	116	3.7	36	47
7	0.039	0.37	0.59	166	2.3	22	36
8a	0.034	0.41	0.56	131	2.6	31	43
8b	0.038	0.38	0.58	216	1.8	18	27
9	0.018	0.47	0.51	166	1.1	28	31
10	0.080	0.43	0.49	402	1.9	10	12

[a] Fluorescence quantum yield, error ± 10% of the stated values. [b] Quantum yield of azoalkane disappearance, error ± 10% of the stated values. [c] Quantum yield of radiationless deactivation, calculated from $1 - [\Phi_r + \Phi_f]$. [d] Fluorescence lifetime, error ± 5% of the stated values. [e] Rate constant of fluorescence. [f] Rate constant of azoalkane disappearance. [g] Rate constant of radiationless deactivation. [h] In benzene, cf. ref 8.

for this puzzling structural feature? Presumably steric effects operate, which have been diagnosed by semiempirical calculations (AM1). The structural influence of the annelated ring systems is displayed in the minimum-energy structures shown in Figure 1. In the case of the norbornyl-substituted azoalkane **3a**, the azo chromophore is more effectively shielded when compared to the cyclopropyl-substituted derivative **1**. It is known from our previous work that such steric shielding in azoalkane **3a** reduces the efficiency of the fluorescence quenching by olefins compared to that of substrate **1**.[10] This is due to less effective exciplex formation during the quenching process as steric repulsion between the azoalkane and the quencher increases.[10,11] In the present case, the quencher is the solvent, whose effective interaction with the n,π*-excited azo chromophore is sterically encumbered; hence, the solvent-induced quenching of the fluorescence is reduced and thereby the fluorescence lifetime is increased. The fact that the fluorescence properties Φ_f and τ of the mixed cyclopropyl- and norbornyl-annelated azoalkane **2** fall almost exactly between those of **1** and **3a** (Table 1) corroborates that steric effects operate. Moreover, replacement of the cyclopropyl hydrogen atoms in substrate **1** by methyl groups, as in the derivative **4**, also enhances the fluorescence efficiency (Φ_f) and lifetime (τ) about 10-fold (Table 1), which may only be reconciled in terms of effective steric shielding from above. In a similar manner, the benzvalene annelation in **7** shields the azo chromophore also very effectively; consequently, the fluorescence lifetime increases to 166 ns. As expected, shielding from below (compare **1**, **5** and **2**, **6**) does not significantly influence the fluorescence properties (Table 1).

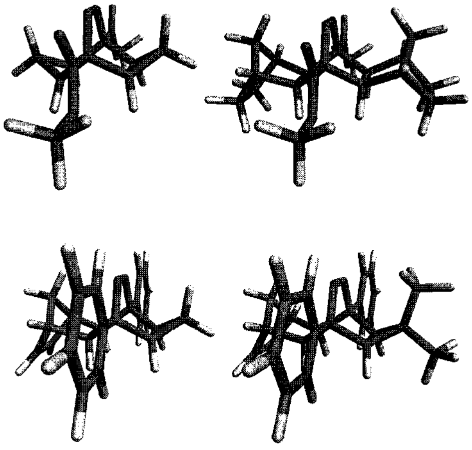

Figure 1. Minimum-energy structures of the ester-substituted azoalkanes **1** and **3a** (above) and the phenyl-substituted ones **8b** and **10** (below), as calculated by the semiempirical AM1 method.

Phenyl-Substituted Azoalkanes. In the phenyl-substituted azoalkanes **8b**, **9**, and **10** there are similar trends to observe. Analogous to the already described ester-substituted derivatives **1**, **2**, and **3** (the double bond in the norbornene ring has only a nominal influence on the photophysical properties, compare the ester derivatives **2** and **8a**), the fluorescence intensities (Φ_f) and lifetimes (τ) depend significantly on the steric accessibility of the azo chromophore. The unexpectedly high fluorescence lifetime of **10** (402 ns) is especially remarkable. Again, this long lifetime may be explained in terms of the excellent steric shielding of the azo group by the norbornyl- (**8b**, **9**, **10**) and the *gem*-dimethyl-substituted cyclopropyl (**10**) groups. The semiempirically computed

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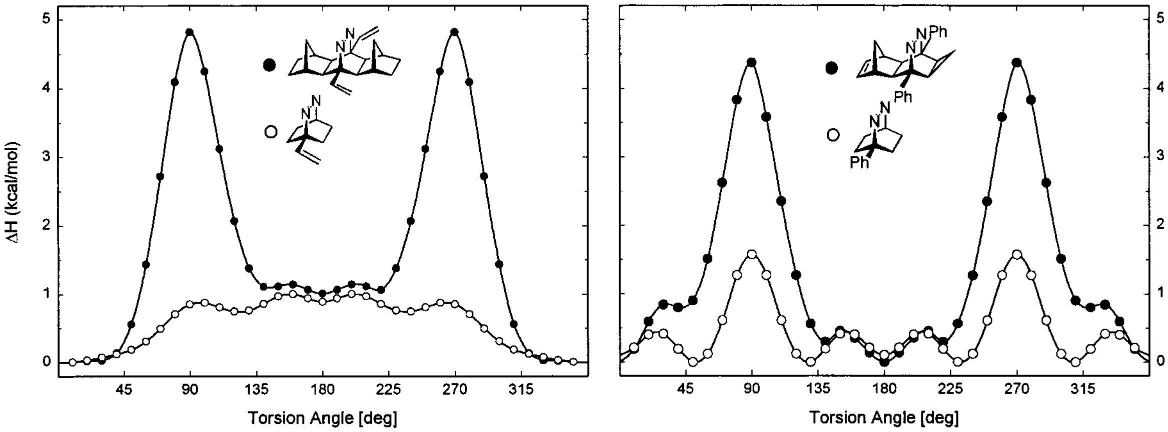


Figure 2. Rotational barrier of the vinyl group in the azoalkanes **3d** and Vi-DBO (left) and the phenyl group in the azoalkanes **8b** and Ph-DBO (right), as calculated by the semiempirical AM1 method.

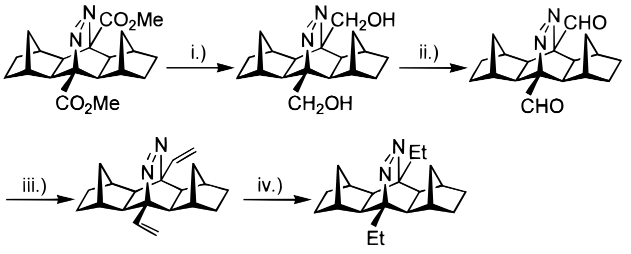
minimum-energy structures of the derivatives **8b** and **10** are shown in Figure 1.

As in the ester-substituted case, there is no significant influence of ring annelation on the photoreactivities (Φ_r). Nevertheless, at first glance the photoreactivity of the phenyl-substituted azoalkanes seems to be unexpectedly low ($\Phi_r = 0.38-0.47$) compared to that of Ph-DBO (Table 1), since the latter exhibits a quantum yield of unity ($\Phi_r = 1$). This behavior is based on steric interactions between the *o*-phenyl and the bridgehead-norbornyl hydrogen atoms in the annelated derivatives **8b**, **9**, and **10**. In these cases, the rotational energy barrier to reach the required optimal conformation for efficient radical stabilization (90°, 270°) is about three times higher than that in the Ph-DBO system (Figure 2, right). Thus, the efficiency of the nitrogen extrusion (Φ_r) is decreased because the incipient carbon-radical site of the diazenyl diradical is less stabilized.

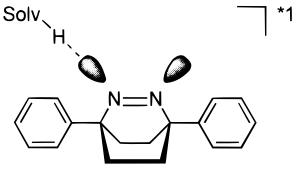
In the ester-substituted azoalkanes **1**, **2**, and **3a** the rotational barriers of the ester groups are all below 1.5 kcal/mol and, therefore, not higher than in the Ph-DBO case. Consequently, the radical-stabilizing conformation is readily accessible and such conformational alignment for optimal delocalization is not important for the ester derivatives.

It is noteworthy that the nearly perpendicular conformational alignment of the phenyl groups introduces an even more effective shielding of the azo chromophore than in the ester-substituted case (Figure 1). Not only steric shielding by the annelated rings from above but also by the phenyl groups operates, i.e., skew attack by solvent molecules from above along the perpendicularly aligned phenyl group. This behavior is especially important in view of the recent experimental and theoretical work by Nau on the deactivation mechanism of singlet-excited DBO.[12] The interaction of solvent C−H bonds with the nonbonding orbitals of the azo nitrogen atoms with partial H transfer has been proposed for effective quenching, as illustrated in structure **A** for the phenyl derivative **8b**. Consequently, the higher singlet lifetime of **8b** (216 ns) compared to that of the ester-substituted **8a** (131 ns) may be explained in terms of this novel mechanism. Moreover, these extraordinarily long lifetimes of the singlet excited state yield remarkably low rate constants of azoalkane disappearance and fluorescence (Table 1).

Scheme 1



i.) LiAlH$_4$, THF, ca. 20 °C, 30 min. - ii.) 1. ClCOCOCl, DMSO, CH$_2$Cl$_2$, -60 °C, 10 min, 2. NEt$_3$, -60 °C, 15 min. - iii.) Ph$_3$P=CH$_2$, THF, ca. 20 °C, 18 h. - iv.) H$_2$, Pd/C, toluene, ca. 20 °C, 24 h.



A

Azoalkanes with Other Bridgehead Substituents. The synthetic procedures for the preparation of the new azoalkanes **3b**−**3e** are summarized in Scheme 1. Due to the insolubility of the hydroxymethyl derivative **3b** in MeCN, no photophysical data were measured for this compound.

Effects similar to those of the phenyl-substituted azoalkanes operate in the case of the vinyl-substituted azoalkane **3d**. Although the vinyl group facilitates the extrusion of nitrogen due to the stabilization of the incipient radical site, its photoreactivity ($\Phi_r = 0.67$) is appreciably lower than that of Vi-DBO ($\Phi_r = 1$). Again, conformational effects are responsible: The torsional barrier for the rotation of the vinyl group to reach the optimal radical-stabilizing conformation (90°, 270°) is much larger for **3d** than Vi-DBO (Figure 2, left side), which accounts for the decreased photoreactivity. The good steric shielding of the azo chromophore by the norbornyl groups (top attack) and by the nearly perpendicularly aligned vinyl groups (skew attack) is responsible for the remarkably high fluorescence lifetime and efficiency.

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The photoreactivity of the dialdehyde **3c** is appreciably higher than that of the diester **3a** because CH═O stabilizes a radical site better than CO_2Me;[13] moreover, semiempirical calculations reveal that the rotational hindrance in **3a** and **3c** is much lower than in **3d**, such that the optimal conformations for effective delocalization may be populated. Consequently, due to the higher photoreactivity, the fluorescence efficiency and lifetime of **3c** are decreased compared to those of **3a**.

The ethyl-substituted azoalkane **3e** constitutes the most photoreluctant case examined herein ($\Phi_r = 0.0090$). Since the ethyl group, compared to the other substituents, stabilizes a radical center only nominally, it does not facilitate nitrogen extrusion. Its extraordinarily low photoreacivity is accompanied by a high fluorescence quantum yield (the highest of all new azoalkanes in Table 1) and lifetime.

Conclusions

Polycyclic DBO derivatives with radical-stabilizing groups located at the bridgehead positions, i.e., α to the azo chromophore, possess increased photoreactivity (Φ_r) when compared to the parent DBO system and, therefore, exhibit reduced fluorescence efficiencies. *Endo* annelation has no significant influence on the photoreacivity, except when steric effects hinder the α substituent from aligning conformationally with the incipient radical center for good delocalization. Additionally, steric shielding of the azo chromophore by the annelated rings and the bridgehead substituents reduce the solvent-induced quenching of the n,π*-excited state and, thus, the fluorescence quantum yields Φ_f and lifetimes τ are markedly increased.

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Supporting Information Available: Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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