Fluorescence Quenching of Ester-Substituted DBO-Type Azoalkanes by Olefins and Arenes: Electronic and Steric Effects, Exciplex Formation and Hydrogen Abstraction

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Received May 4, 1998

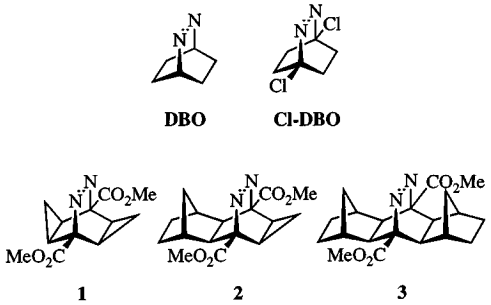
Keywords: Azoalkanes / DBO / Fluorescence quenching / Exciplexes / Hydrogen transfer

The fluorescence of the **DBO** derivatives **1**–**3** is efficiently quenched by olefins and arenes, exciplex formation and hydrogen transfer operate as quenching mechanisms. The electron-accepting ester groups in the azoalkanes **1**–**3** promote significantly more effective quenching compared to the parent **DBO**. Steric hindrance accounts for the differences in the quenching efficiencies, but electronic effects dominate

Introduction

The photochemistry of diazabicyclo[2.2.2]oct-2-ene (**DBO**) and its derivatives has been thoroughly studied in the last three decades and their photophysical behavior was the topic of intensive experimental and theoretical investigations.[1] In contrast to the diazabicyclo[2.2.1]hept-2-ene (**DBH**), the photoreactivity of **DBO** is extraordinary low and, therefore, constitutes a *photoreluctant* or *photopersistent* azoalkane.[2] The low photoreactivity is accompanied by a strong fluorescence emission,[1a] which may be efficiently quenched by olefins and arenes.[3][4][5] In regard to the fluorescence-quenching mechanism, much work has been conducted in the past for its elucidation.[4][5] In isooctane, exclusive formation of an exciplex between the azoalkane and the quencher has been proposed to operate,[4] whereas in acetonitrile additionally H-atom transfer occurs with good donors.[5]

Scheme 1



Recently, we have investigated the photophysical behavior of the polycyclic α-substituted azoalkanes **1**−**3**.[6] Their higher photoreactivity compared to **DBO** is due to the radical-stabilizing ester substituents α to the azo chromophore, which results in a fluorescence emission weaker than in the parent **DBO** system. Although the photoreactivity is not appreciably influenced by structural changes, their fluorescence properties depend significantly on the structure of the annelated ring systems. For example, the fluorescence quantum yield (Φ_f) rises in the order **1** (0.0066) < **2** (0.040) < **3** (0.090), accompanied by an increase of the fluorescence lifetime (τ) in the order **1** (9.2 ns) < **2** (139 ns) **3** (273 ns).[6] Since this photophysical behavior has as yet not been fully understood, it was of interest to gain mechanistic insight into the fluorescence process of the azoalkanes **1**−**3**. For this purpose, we have investigated the fluorescence quenching of these **DBO** derivatives to assess the influence of bridgehead substitution and ring annelation. Our present results confirm the general validity of the initially proposed mechanisms, namely exciplex formation and hydrogen abstraction for the fluorescence quenching of **DBO**-type azoalkanes.[5]

Results and Discussion

The rate constants k_q for the fluorescence quenching of the azoalkanes **1**−**3** by olefins (cf. Experimental Section) are given in Table 1 (entry 1−9) and the trends are displayed in Figure 1. The fair linear correlation between the fluorescence quenching constants (log k_q) and the HOMO energies (ionization potentials) of the quenchers establishes exciplex formation.[4b]

A favorable HOMO/LUMO interaction between the olefinic quencher (HOMO) and the azoalkane (LUMO) promotes exciplex formation. Expectedly, fluorescence quenching becomes less efficient with increasing ionization potential (decreasing HOMO energy) of the quencher due to a less effective HOMO/LUMO interaction; actually, the interaction between the HOMO of the olefin and the SOMO of the excited azoalkane should be considered in the formation of an exciplex, but the qualitative trends are the same.

  1434−193X/98/1010−2177 $ 17.50+.50/0

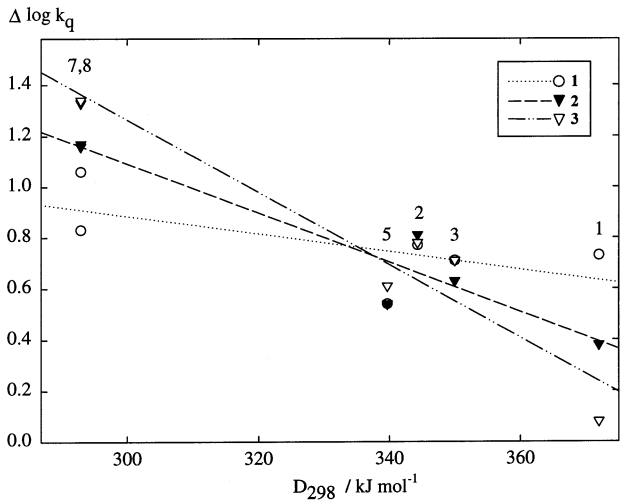
Table 1. Fluorescence quenching of the azoalkanes **DBO** and **1−3** for olefinic and arene quenchers

Entry[c]	Quencher	*IP* [eV][d]	k_q [10^7 M^{-1}s^{-1}][a][b] **1**	**2**	**3**	**DBO**[e]
1	1-hexene	9.45	2.6	0.54	12	
2	cyclopentene	9.02	9.8	3.6	1.3	
3	cyclohexene	8.95	10	2.7	1.2	0.19
4	norbornadiene	8.60	4.1	1.4	0.45	
5	cyclopentadiene	8.57	22	5.2	1.9[f]	
6	styrene	8.44	13	1.9	0.58	0.30
7	1,4-cyclohexadiene	8.40	67	41	14	1.7
8	1,3-cyclohexadiene	8.25	193	40	17	3.2
9	*trans*-stilbene	7.60	112	12	2.6	1.4
10	*p*-dimethoxybenzene	7.90	14	6.3	0.63	0.27[g]
11	*p*-dicyanobenzene	9.70	(1−3)[h]	1.5	1.1	247[i]

[a] In MeCN, 20°C. − [b] Obtained from Stern−Volmer analysis, λ^{ex} = 350 nm, n = 5−8, r^2 = 0.961−0.999; the fluorescence lifetimes are: 9.2 ns (**1**), 139 ns (**2**), 273 ns (**3**). − [c] Correspond to the numbers in Figure 1. − [d] Ionization potential of the quencher, cf. ref.[4b]. − [e] Values for **DBO**, cf. ref.[5]. − [f] For [D_6]cyclopentadiene k_q = 0.63, k_q^H/k_q^D = 3.0. − [g] For **Cl-DBO** k_q = 147, cf. ref.[5]. − [h] No exact value available because of the low fluorescence efficiency of **1** and the strong emission of the quencher. − [i] No quenching observed for **Cl-DBO**, cf. ref.[5].

The pronounced deviations from the expected linear plot in Figure 1 implicate that exciplex formation is not the only mechanism involved in the quenching process. For example, a linear plot applies for the poor hydrogen donors such as *trans*-stilbene (entry 9), styrene (entry 6), and norbornadiene (entry 4), while all other olefins quench the azoalkane fluorescence more efficiently as expected for exciplex formation (Table 2). The biggest deviations, i.e. most efficient fluorescence quenching, are observed for the good hydrogen donors 1,4- and 1,3-cyclohexadiene (entry 7 and 8), while for the moderate hydrogen donors cyclohexene or cyclopentene (entry 2 and 3) smaller deviations are displayed. Indeed, the reasonably good correlations (Figure 2) between the C−H bond strengths of the hydrogen donors versus the deviations from linearity (Figure 1) in the quenching rate constants ($\Delta \log k_q$) provides experimental evidence that additionally the hydrogen-transfer mechanism operates in the fluorescence quenching process. Moreover, a kinetic isotopic effect of k_q^H/k_q^D = 3.0 for the fluorescence quenching of azoalkane **3** (entry 5) by cyclopentadiene versus [D_6]cyclopentadiene, which is in good agreement with the reported values of 1.7 and 3.0 for **DBO**,[5] unequivocally corroborates H abstraction.

Figure 2. C−H bond strengths (D_{298}) versus $\Delta \log k_q$ of the H donors for the azoalkanes **1−3**



The results in Figure 1 display that all olefins quench the fluorescence of the azoalkanes **1−3** more efficiently than that of **DBO**. The common feature of the three **DBO** derivates **1−3** is ester substitution at both bridgehead positions. The electron-accepting ester groups α to the azo chromophore lower the LUMO energy of the latter and thereby enhance the HOMO/LUMO interaction between the olef-

Figure 1. Fluorescence quenching constants of the azoalkanes **DBO** and **1−3** versus the IPs of the olefinic quenchers

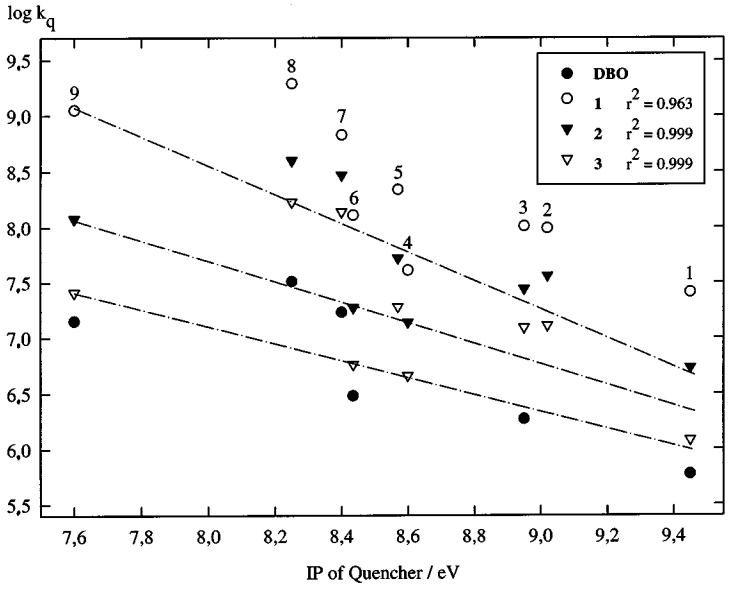


Table 2. C−H bond strengths and deviations of linearity of the H donors in Figure 1

Entry[b]	Quencher	D_{298} [kJ/mol][c]	Δ log k_q[a] **1**	**2**	**3**
1	1-hexene	372	0.73	0.38	0.08
2	cyclopentene	344	0.77	0.81	0.78
3	cyclohexene	350	0.71	0.63	0.71
5	cyclopentadiene	340	0.54	0.54	0.61
7	1,4-cyclohexadiene	293	0.83	1.16	1.33
8	1,3-cyclohexadiene	293	1.06	1.17	1.34

[a] Deviations from linearity in Figure 1. − [b] Corresponds to the entries in Table 1 and Figure 1. − [c] C−H bond strengths at 298 K, cf. ref.[7].

inic quencher and the azoalkane; consequently, the quenching efficiency is increased through more effective exciplex formation. Additional experimental evidence provide quenching experiments with electron-rich and electron-poor arenes (Table 1; entries 10, 11). Thus, the electron-rich *p*-dimethoxybenzene quenches the fluorescence of the azoalkanes **1−3** more efficiently than that of **DBO**, while for the electron-poor *p*-dicyanobenzene quenching is much less efficient than for the **DBO** case. This photophysical behavior is similar to that observed previously for **Cl-DBO**,[5] although its fluorescence is not quenched by *p*-dicyanobenzene. This difference between **Cl-DBO** and the azoalkanes **1−3** may be rationalized by comparison of the group electronegativities of the chloro (3.0) and ester (2.8)[8] substituents.

Besides these electronic effects, also steric effects operate. Since exciplex formation is known to be sensitive to steric hinderance,[4a] the differences of the fluorescence quenching efficiencies for the azoalkanes **1−3** (Table 1) may be accounted for in terms of the ease of access of the quencher to the excited azo chromophore. Compared to cyclopropyl, the larger norbornyl group shields the azo chromophore more effectively and, thereby, lowers the interaction with the quencher. Nevertheless, it should be noted that in the present case of the **DBO** derivatives **1−3**, the electronic effects surpass clearly the steric ones. Thus, the fluorescence quenching of the azoalkanes **1−3** is more efficient than for **DBO**, although their azo chromophores are sterically more shielded than in **DBO**.

Conclusions

The fluorescence of the ester-substituted azoalkanes **1−3** is efficiently quenched by electron-rich olefins and arenes. Analogous to the parent **DBO**,[5] exciplex formation and hydrogen transfer operates as quenching mechanism in acetonitile. The electron-accepting ester groups in these **DBO** derivatives promote significantly more effective quenching compared to **DBO**. Steric hinderance accounts for the differences in the quenching efficiencies of the azoalkanes **1−3**, but electronic effects dominate.

Generous financial support from the *Volkswagenstiftung*, the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* are gratefully appreciated.

Experimental Section

General: Spectrophotometric grade (Fluka) acetonitrile was used as purchased. The azoalkanes **1−3** were prepared according to the literature procedures[9] and recrystallized before use. The olefins and arenes were purified by recrystallization or distilled immediately before use. The steady-state fluorescence spectra were recorded with a Perkin-Elmer LS50 luminescence spectometer. The fluorescence lifetimes for the calculation of k_q values were determined with a single-photon-counting apparatus from Edinburgh Instruments by excitation of sealed, degassed azoalkane solutions at 358 nm.

Fluorescence Quenching: Azoalkane solutions were carefully degassed by at least three freeze-pump-thaw cycles. The quenching rate constants were determined by the Stern−Volmer method from intensity measurements of the azoalkane solutions (λ^{ex} = 350 nm, λ^{em} = 365−600 nm) with and without quenchers (c = 0−0.20 mmol/l, n = 5−8, r^2 = 0.961−0.999) under argon gas at 20°C.

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