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CONJUGATED DIENES AS QUENCHERS OF THE FLUORESCENCE OF 2,3-DIAZABICYCLO[2,2,2]OCT-2-ENE

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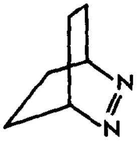
Conjugated dienes quench singlet-excited states of aromatic hydrocarbons (1) and azoalkanes (2). The process is generally less efficient than triplet quenching by dienes, and its nature is still somewhat obscure. We have studied the quenching of the fluorescence of the azo-compound (I) by dienes, and report here the effect of structure on quenching efficiency.

Stern-Volmer plots for quenching in deoxygenated hexane at 25° were linear up to at least 0.8M diene. The bimolecular quenching rate-constants (k_q) in the Table were calculated from the Stern-Volmer gradients (τk_q) and an assumed singlet lifetime of 3.3×10^{-7} sec.*



(I)

The Table shows that the introduction of methyl groups into acyclic dienes (A-K) increases quenching efficiency, terminal substitution being in most cases more effective than 2- or 3-substitution. The 3-alkylidenecyclohexenes (L-Q) show similar effects: compare L with N and O; M with Q; N with O. However, several dienes do not follow the general trend, and it seems that steric effects of two kinds are operative.

(i) The introduction of gem-dimethyl groups at saturated sites in methylenecyclohexenes reduces efficiency markedly: compare L with M; O with P. This suggests that, as for naphthalenes (1),

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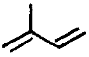
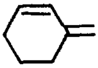
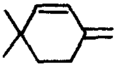
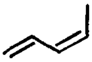
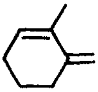
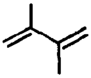
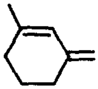
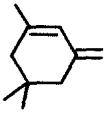
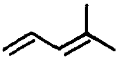
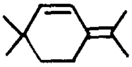
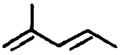
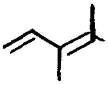
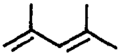
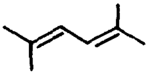
[*] As found in iso-octane at 25° (3). If the lifetime in hexane differs from this, the rate constants will all be affected by a constant factor: structure-quenching efficiency correlations will thus still be valid. Quenching constants in iso-octane have recently been reported (4) for piperylene, cyclopentadiene, and cyclohexadiene (3.0, 5.6, and 25.6 x 10^7 l.mole^{-1} sec.$^{-1}$, respectively).

TABLE

Quenching of Diazabicyclo-octene (I) Fluorescence by Dienes

	Diene	$10^{-7}k_q$[*]		Diene	$10^{-7}k_q$[*]
A		1.36	L		5.93
B		1.18	M		2.19
C		2.33	N		8.74
D		1.83	O		36.5
E[+]		3.54	P		9.22
F		4.64	Q		29.1
G		2.69	R		3.43
H		5.08	S		10.9
J		1.85	T		1.23
K		10.7			

[*] l.mole^{-1}sec.$^{-1}$

[+] Mixture of isomers

fluorescence quenching by dienes requires very close contact between the azo-compound and the quencher.

(ii) Diene J is less efficient than dienes F and G; probably the extra methyl group in J reduces quenching efficiency by preventing planarity of the diene. The methylenecyclohexene O, a diene of the same substitution type as J yet lacking this unfavourable steric factor, is 20 times as efficient as J.

With the available results, there seems to be no large intrinsic difference in efficiency between cisoid and transoid dienes. Cyclohexa-1,3-diene S is 3 times as efficient as its acyclic counterpart E, but a comparable enhancement (X2) is found in the transoid diene L relative to G. The greater efficiency of such cyclic systems may be due simply to their necessary planarity or near-planarity.[**] *cis,cis*-Cyclo-octa-1,3-diene T provides an example of a cyclic diene which is inefficient because it is necessarily non-planar. On this basis, the difference between cyclohexadiene S and cyclopentadiene R is surprising; it may be related to the angle strain in the latter and/or to differences in spectroscopic behaviour (absorption maxima: S, 257; R, 239 mμ).

Cyclohexene, norbornadiene, benzene, and furan were poor quenchers compared to the conjugated dienes, as were molecules containing heavy atoms (methyl iodide, n-propyl bromide). The lack of a heavy-atom effect could imply that the function of the quencher is not necessarily to facilitate intersystem crossing, though such an effect might well be negligible for an $(\underline{n},\pi^*)$ state (5).

The sensitivity of k_q to diene substitution probably reflects a relationship between quenching efficiency and the singlet excitation energies of the dienes, the observed $k_q/\lambda_{max.}$ correlations (cf. dienes R and S, above) being of a similar kind to those found (1) in the case of aromatic hydrocarbons. It is also relevant that the absorption and emission spectra of diazabicyclo-octene were not significantly affected by the presence of dienes, and also that the dienes underwent no detectable reaction during quenching. Hammond's model, *viz.* the catalysis of radiationless decay through an excited complex ("exciplex") of substrate and quencher (1), seems at present to offer the simplest interpretation of our results.

[**] Comparison of *trans*- and *cis*-piperylene (B and C) could, however, imply that *cis*-substituted acyclic dienes are *intrinsically more* efficient than their *trans*-isomers in quenching *excited* (I). A better model for methylenecyclohexene would then be *the cis*-isomer of G; likewise the model for cyclohexadiene would be the pure *cis,cis*-isomer of E. *It is* possible that, relative to such models, the enhancements found for the *cyclic* dienes L and S will disappear. Studies are under way to test this point. Other effects discernible in the Table will be discussed in detail later.

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