

Direct and Sensitized Geometrical Photoisomerization of 1-Methylcyclooctene

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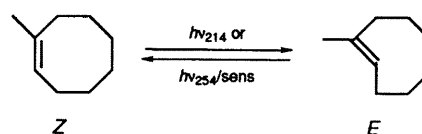
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Effects of methylation at C(1) of cyclooctene on the ground-state structure, potential energy surfaces, and photochemical behaviour in the singlet and triplet manifolds have been investigated. Molecular mechanics calculations using the MM2 force field reveal that, as compared with the parent (*E*)-cyclooctene, methylation increases the strain of the (*E*)-isomer by 8.9 kJ mol⁻¹, which is however released in part through the minimized steric repulsion between one of the ring methylenes and the introduced methyl by increasing the dihedral angle C(Me)-C(1)=C(2)-C(3).

Direct excitation at 214 nm of 1-methylcyclooctene does not lead to the Rydberg state-derived rearrangement products, but results in efficient geometrical isomerization, affording a photostationary *Z*-*E* mixture upon prolonged irradiation. From the photostationary state *E/Z* ratio observed [(*E/Z*)_{ps} = 0.30] and the excitation ratio ($\epsilon_Z/\epsilon_E = 0.305$) calculated from the extinction coefficients (ϵ) at 214 nm of both isomers, we obtain the decay ratio (k_{dE}/k_{dZ}) of 0.98 for the singlet-excited 1-methylcyclooctene (¹p). This ratio, being close to that of cyclooctene ($k_{dE}/k_{dZ} = 0.88$), means equal-probability decay from ¹p to highly strained (*E*)-isomer and less-strained (*Z*)-isomer. Somewhat unexpectedly, triplet sensitization with aromatic hydrocarbons gave only slightly higher (*E/Z*)_{ps} values of 0.03–0.26 than the corresponding values for cyclooctene, indicating that the crossing profiles of the triplet and ground-state surfaces of 1-methylcyclooctene resemble each other, in spite of the increased strain in the (*E*)-isomer. By contrast, the singlet sensitization was shown to be very sensitive to the steric hindrance of the sensitizer. As compared with the cyclooctene case, the less congested benzoate gives almost the same (*E/Z*)_{ps} ratio, whereas the use of more congested benzenepolycarboxylates results in much decreased ratios. This drastic difference between triplet and singlet sensitizations may be rationalized in terms of the intervention of an exciplex in the singlet sensitization, which provides stronger and longer mutual interaction between sensitizer and substrate. The singlet-sensitized photoisomerization has been used as a convenient one-step route to the highly constrained (*E*)-1-methylcyclooctene.

Geometrical photoisomerization of cycloalkenes, and the subsequent thermal reactions of the constrained (*E*)-isomers generated, have enabled us to understand the unusual photochemical behaviour and the enhanced thermal reactivities arising from the constrained structure and the deformed potential energy surfaces.^{1–21} Highly constrained, but still moderately stable, (*E*)-cyclooctene has been used frequently as a representative model compound in theoretical^{3–7} and experimental investigations.^{2,8–18} From the studies on the photochemistry of cyclooctene in the singlet and triplet manifolds,^{13–18} we have demonstrated that, in sharp contrast to the constant photostationary state *E/Z* ratio [(*E/Z*)_{ps}] around unity for acyclic alkenes, the (*E/Z*)_{ps} ratio of cyclooctene is highly sensitive to the excitation mechanism and the excited state involved. Thus, the direct excitation of cyclooctene at 185 nm in pentane gives an (*E/Z*)_{ps} value of 0.98,^{13,14} which is analogous to those obtained for acyclic alkenes. On the other hand, the triplet sensitization with aromatic hydrocarbons affords varying (*E/Z*)_{ps} ratios of 0–0.22,^{14,16,17} depending upon the sensitizer's triplet energy (*E*_T), while the singlet sensitization with aromatic carboxylates gives much higher ratios up to 0.7 *via* an exciplex,^{15,18} the intervention of which has been proved by the efficient enantiodifferentiating photoisomerization sensitized by several chiral aromatic esters.^{22,23}

In the present paper, a methyl group is introduced to cyclooctene at C(1), and its steric and electronic effects on the potential energy surfaces and the photochemical behaviour upon direct excitation at 214 nm and triplet and singlet sensitizations, are elucidated in comparison with those of unsubstituted cyclooctene.



Scheme 1

Experimental

General.—Infrared spectra were obtained on a JASCO IR-810 instrument. ¹H and ¹³C NMR spectra were recorded on a JEOL GX-400 spectrometer, using [²H]chloroform as solvent. *J* Values are in Hz. Electronic spectra in vapour and solution phases were recorded in a stoppered quartz cell (10 × 10 × 45 mm) at wavelengths >190 nm on a JASCO Ubest-50 spectrometer. Gas chromatographic (GC) analyses were performed using a Shimadzu 6A instrument.

Materials.—All aromatic hydrocarbons and carboxylic esters employed as sensitizers, which were commercially available or synthesized independently, were purified by fractional distillation or repeated recrystallization from methanol. Pentane used as a solvent was stirred over concentrated sulfuric acid until the acid layer no longer turned yellow, washed with water, neutralized with aq. sodium hydrogen carbonate, dried over magnesium sulfate, and then distilled fractionally.

(*Z*)-1-Methylcyclooctene was synthesized by the reaction of cyclooctanone with methylmagnesium iodide, followed by spontaneous dehydration upon distillation of the crude

Table 1 Electronic spectra of (*Z*)- and (*E*)-1-methylcyclooctenes in pentane

1-Methylcyclooctene	Onset/nm	λ_{\max}/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$\epsilon(214 \text{ nm})/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
(<i>Z</i>)-Isomer	222	198 (9280)	1710
(<i>E</i>)-Isomer	240	203 (6930)	5610

product, according to the procedures reported by Brown and Borkowski.²⁴

(*E*)-1-Methylcyclooctene was prepared from its (*Z*)-isomer through the singlet-sensitized photoisomerization. A solution of 7.45 g (60 mmol) of (*Z*)-1-methylcyclooctene and 0.41 g (3 mmol) of methyl benzoate in 300 cm³ of pentane was placed in an annular quartz vessel, bubbled with argon gas, and then irradiated for 25 h at 25 °C, using a 30 W low-pressure mercury lamp (Eikosha) fitted with a Vycor sleeve, until an apparent photostationary state [(*E*/*Z*)_{ps} = 0.20] was reached. The photolysate was extracted at 0 °C with three 60 cm³ portions of 10% silver nitrate solution in methanol–water (3:4 v/v). The combined methanol–water extracts (180 cm³) were diluted with 175 cm³ of water, washed with two 25 cm³ portions of pentane, and then added dropwise into a stirred mixture of pentane (25 cm³) and 28% aqueous ammonia (100 cm³). The temperature was kept below 5 °C throughout these procedures. The resulting mixture was extracted with three 25 cm³ portions of pentane, and the combined pentane extracts were washed with water, dried over magnesium sulfate, and concentrated at reduced pressure, and then bulb-to-bulb distilled *in vacuo* to afford pure (*E*)-1-methylcyclooctene (0.51 g, 6.9% yield): $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3040, 2910 (s), 2850 (s), 1450 (s), 1380, 1200 (m), 990, 980, 925, 875 (m), 845, 810, 750, 700, 560, 525; $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 0.65 (dt, *J* 6.1, 13, 1 H), 0.90 (dt, *J* 5.9, 13, 1 H), 1.42 (dq, *J* 5.4, 12.2, 1 H), 1.57–1.70 (m, 3 H), 1.74 (d, *J* 1.2, 3 H, CH₃), 1.84 (br d, *J* 12.2, 1 H), 1.89–1.97 (m, 1 H), 2.06 (dt, *J* 4.6, 11.9, 1 H), 2.13–2.31 (m, 3 H), 5.38 (dd, *J* 1.2, 11.5, 1 H, CH=); $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 18.19, 27.90, 30.25, 30.98, 33.48, 36.75, 41.69, 127.19 (CH=), 137.69 (MeC=).

Photolysis.—All irradiations were run in a temperature-controlled water bath at 25 °C. Photosensitizations were carried out in quartz tubes under argon atmosphere at 254 nm using a 30 W low-pressure mercury lamp (Eikosha) fitted with a Vycor sleeve. Direct photolyses were performed in Suprasil tubes at 214 nm of a zinc resonance lamp (Philips).

Gas chromatographic analyses of photolysates were performed over a 3 m column of 20% polyethylene glycol-300 at 65 °C (injection port temperature: 100 °C). (*E*)-1-Methylcyclooctene was shown to be totally stable under the analytical conditions. (*Z*)- and (*E*)-1-methylcyclooctenes and cyclooctane, added as an internal standard, were separated satisfactorily under these conditions.

Results and Discussion

Molecular Mechanics Calculation.—In order to evaluate the structural and energetic effects of the methyl substitution on cyclooctene's eight-membered ring, the optimized structures and strain energies of (*Z*)- and (*E*)-1-methylcyclooctene, as well as the parent compounds (*Z*)- and (*E*)-cyclooctene, were calculated by using the Allinger's MM2 program partly modified by Osawa.^{25,26} The structures were fully optimized by starting with several different initial conformations and utilizing MM2's drive option to find the global minimum.

The optimized structures and steric energies for (*Z*)- and (*E*)-isomers of cyclooctene and 1-methylcyclooctene are illustrated

comparatively in Fig. 1; the results for cyclooctenes are in good agreement with those reported by Allinger and Sprague.⁶ It is noted that the introduction of a methyl group does not significantly affect the global conformation of the (*Z*)-isomer, while some moderate deformations around the double bond are induced in the (*E*)-isomer. Thus, methylation only slightly alters the bond length of C(1)=C(2) from 1.340 to 1.343 Å and the dihedral angle of C(8)–C(1)–C(2)–C(3) from 145.3 to 144.8°. However, a more unequivocal change, from 171.1 to 175.8°, is found between the dihedral angle H(1)–C(1)–C(2)–H(2) of cyclooctene and C(Me)–C(1)–C(2)–H(2) of 1-methylcyclooctene. In other words, the steric hindrance caused by methylation is released in part by minimizing steric repulsion between one of the ring methylenes and the introduced methyl. Nonetheless, the overall steric energy difference (ΔSE) between (*Z*)- and (*E*)-1-methylcyclooctene amounts to 49.0 kJ mol⁻¹ which is 8.9 kJ mol⁻¹ greater than that for the parent cyclooctene.

Electronic Spectrum.—Absorption spectra of (*Z*)- and (*E*)-1-methylcyclooctene were measured in the vapour and solution phases. The vapour-phase spectra, shown in Fig. 2(a), clearly exhibit sharp spikes of the $\pi, R(3s)$ Rydberg band around 200 nm overlying a broad continuum of the π, π^* transition band. The (*Z*)- and (*E*)-isomers show substantially different absorption onsets of 222 and 240 nm, respectively, which are shifted to longer wavelengths by 10–15 nm as compared with those of the parent (*Z*)- and (*E*)-cyclooctene. From the difference in the onset wavelengths of (*Z*)- and (*E*)-1-methylcyclooctene, one can evaluate the singlet-energy difference (ΔE_s) of both isomers as 40.6 kJ mol⁻¹, which is almost comparable to the ΔSE value calculated above.

As can be seen from Fig. 2(b), the measurements in pentane solutions gave similar but more diffused absorption spectra for both isomers, in which the spikes assigned to the Rydberg transition are absent, although the peak maxima and onsets are analogous to those in the vapour phase. The relevant data are summarized in Table 1.

Potential Energy Curve.—Taking into account the potential energy curves for cyclooctene proposed previously¹⁴ on the basis of those for ethylene,²⁷ and the above spectral data and calculated energies, we deduced the potential energy curves for 1-methylcyclooctene in the ground and excited states. In Fig. 3, the estimated potential curves for the ground (*S*₀), excited singlet (*S*₁), and triplet (*T*₁) states of 1-methylcyclooctene are shown in solid lines, and those for cyclooctene in dashed lines, where the energy is normalized for the (*Z*)-isomers in *S*₀. As exemplified amply in the literature^{1,28} and indicated by the bathochromic shift of onset observed in the present case, the introduction of a methyl group considerably reduces the energies of the *S*₁ and probably the *T*₁ states. Hence, the potential curves for *S*₁ and *T*₁ are lowered by 20–40 kJ mol⁻¹, while the strain energy of the (*E*)-isomer is increased by 9 kJ mol⁻¹, as shown in Fig. 3.

Direct Photolysis.—Direct irradiations at 214 nm of a pentane solution containing pure (*Z*)- or (*E*)-1-methylcyclooctene (10 mmol dm⁻³) were performed under an argon atmosphere at 25 °C. Periodical monitoring, by GC, of aliquots removed from the photolysate indicated that the major course of the photoreaction is the geometrical *Z*–*E* isomerization at this wavelength and no by-products are detected by GC; the material balance was excellent. The isomer composition, or (*E*)-isomer content, is plotted as a function of irradiation time in Fig. 4. Upon prolonged irradiation, the pentane solution containing each pure isomer gave a common steady-state *E*–*Z* mixture (*E*/*Z* = 0.30 or 23% *E*). This was shown to be the ultimate photostationary state, since the irradiation of an *E*–*Z*

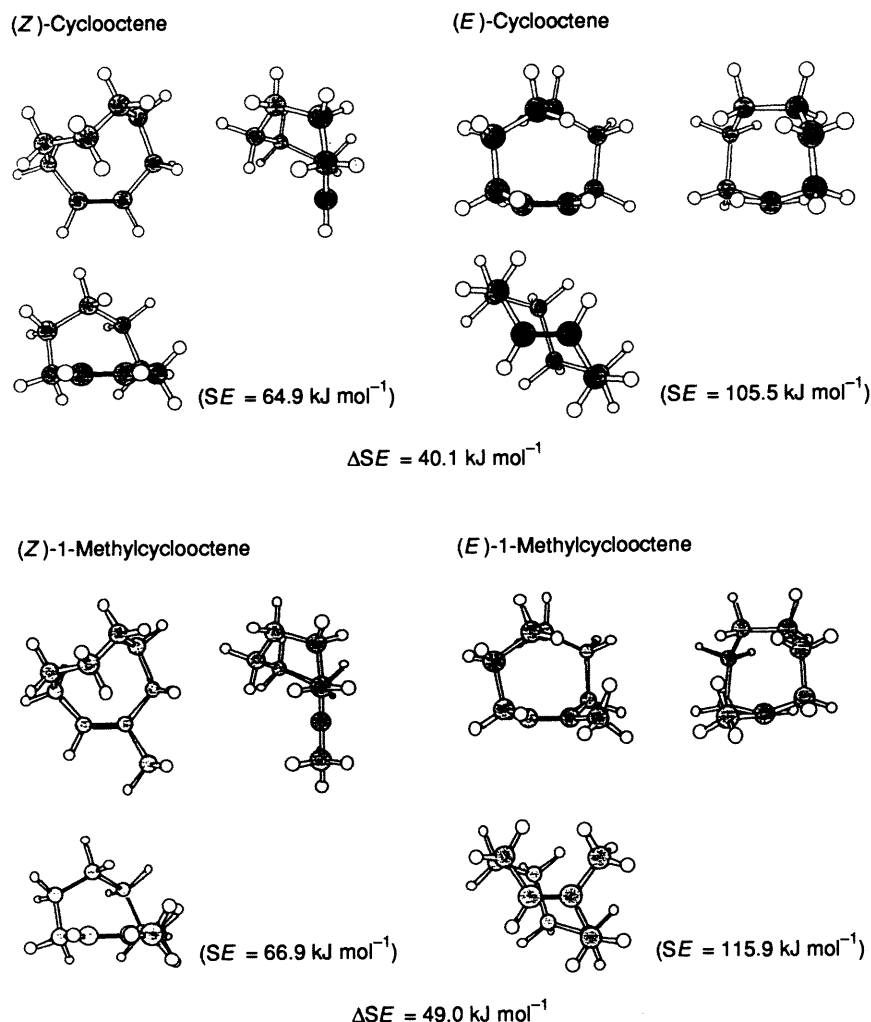


Fig. 1 Top, front, and side views of MM2-optimized structures of (*Z*)- and (*E*)-cyclooctenes and (*Z*)- and (*E*)-1-methylcyclooctenes; steric energies (*SE*) for each conformer are shown in parentheses

mixture of 23% *E*-content showed no appreciable change upon irradiation under the same conditions; see the middle trace in Fig. 4.

Assuming a common twisted singlet intermediate (¹p), the geometrical isomerization of (*Z*)- and (*E*)-1-methylcyclooctenes (**Z** and **E**) upon direct irradiation at 214 nm is described by eqns. (1)–(4) where ϵ_Z and ϵ_E represent the extinction



coefficients of (*Z*)- and (*E*)-1-methylcyclooctene at 214 nm and k_{dZ} and k_{dE} the rate constants for the decay of ¹p to (*Z*)- and (*E*)-isomers, respectively. A steady-state treatment of the above sequence leads to the following expression for the *E/Z* ratio at the photostationary state (pss) [eqn. (5)].

$$(E/Z)_{\text{pss}} = (\epsilon_Z/\epsilon_E)(k_{dE}/k_{dZ}) \quad (5)$$

From the excitation ratio ($\epsilon_Z/\epsilon_E = 0.305$), calculated from the extinction coefficients at 214 nm shown in Table 1, and the observed photostationary ratio [(*E/Z*)_{pss} = 0.30], one can calculate the decay ratio (k_{dE}/k_{dZ}) for the twisted singlet (¹p) of 1-methylcyclooctene as 0.98, using eqn. (5). This decay ratio of almost unity is comparable to that for cyclooctene ($k_{dE}/k_{dZ} = 0.88$) observed upon direct irradiation at 185 nm.¹⁴ The analogous decay ratios obtained for cyclooctene and 1-methylcyclooctene indicate that both *S*₀ and *S*₁ potential curves for these alkenes, though different in energy, are similar in shape, and therefore the relative position of the *S*₀ maximum and *S*₁ minimum is not greatly altered by the methyl substitution, and may justify the estimated potential curves illustrated in Fig. 3.

Triplet Sensitization.—Triplet-sensitized photoisomerizations of 1-methylcyclooctene at varying concentrations of 0.2–30 mmol dm⁻³ were carried out at 25 °C under argon atmosphere in pentane solutions containing alkylbenzene sensitizers (0.1 mol dm⁻³) of different triplet energies (*E*_T) shown in Table 2. The (*E/Z*)_{pss} ratios obtained upon prolonged irradiation with varying substrate concentrations are summarized in Table 2.

It is noted that the (*E/Z*)_{pss} ratio is a critical function of not only the sensitizer *E*_T but also the substrate concentration. As typically exemplified in the benzene sensitization, the

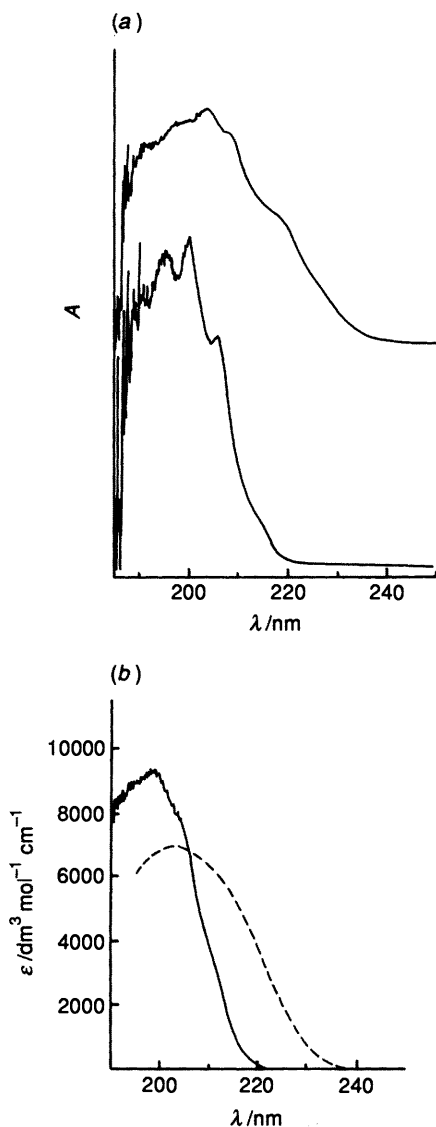


Fig. 2 (a) Vapour-phase absorption spectra of (*Z*)- (lower trace) and (*E*)-1-methylcyclooctene (upper trace); the absorbance is shown in arbitrary units, since the sample pressure was not measured; (b) solution-phase spectra of (*Z*)- (full line) and (*E*)-1-methylcyclooctene (broken line) in pentane

$(E/Z)_{\text{pss}}$ ratio increases with decreasing substrate concentration, approaching a plateau below a certain substrate concentration around 2 mmol dm^{-3} , except for the benzene case. This sort of phenomenon has already been reported and rationalized in the triplet sensitization of cyclooctene,¹⁶ where the lower $(E/Z)_{\text{pss}}$ ratios at higher substrate concentrations are attributed to the operation of singlet sensitization affording much lower $(E/Z)_{\text{pss}}$ ratios owing to the preferential quenching by (*E*)-isomer of the short-lived sensitizer singlet. Hence, the $(E/Z)_{\text{pss}}$ values at 2 mmol dm^{-3} are adopted as the ultimate pss ratios resulting from the pure triplet sensitization except for the benzene case, for which the ratio at 0.5 mmol dm^{-3} is used. In Fig. 5, the $(E/Z)_{\text{pss}}$ ratios thus obtained are plotted as a function of the sensitizer E_{T} , along with those for cyclooctene reported previously.¹⁶ Somewhat unexpectedly, the $(E/Z)_{\text{pss}}$ ratios for 1-methylcyclooctene are only slightly higher than those for the parent cyclooctene, and the profile of E_{T} -dependence is quite similar in both cases.

On the basis of the well-accepted concept¹ and the potential energy curves shown in Fig. 3, the triplet-sensitized *Z*-*E* photoisomerization of simple alkenes is considered to proceed through a common twisted triplet (^3p). Then, the photostationary

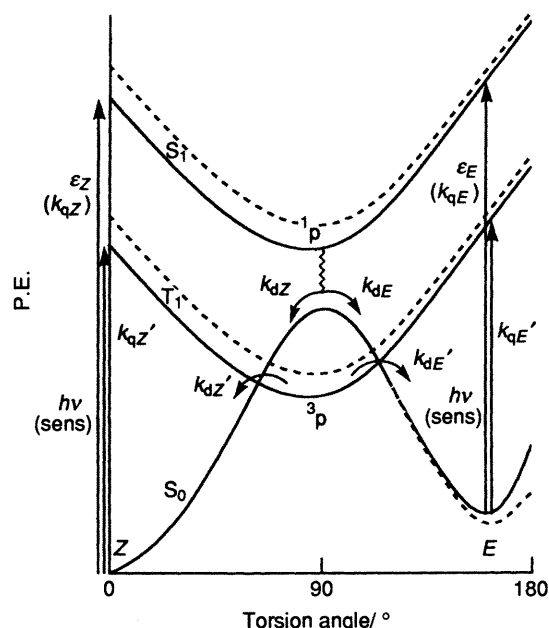


Fig. 3 Potential energy curves for ground (S_0), excited singlet (S_1), and triplet (T_1) states of 1-methylcyclooctene (solid lines), deduced from those for cyclooctene (dashed lines)

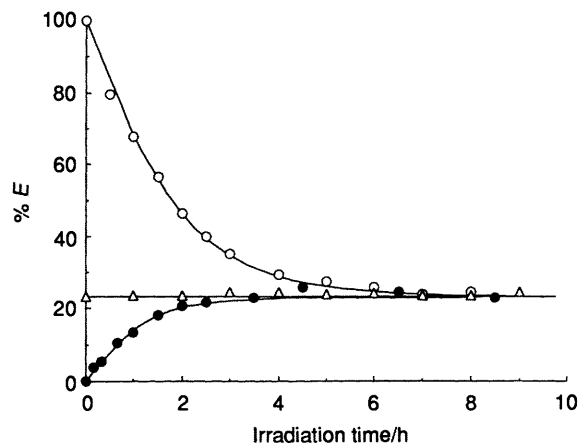


Fig. 4 Direct photoisomerization at 214 nm of 1-methylcyclooctene in pentane, starting with initial isomer compositions of 100% *E* (○), 23% *E* (△) and 0% *E* (●)

E/Z ratio is given as a product of the excitation ratio (k_{qZ}/k_{qE}) and the decay ratio (k_{dE}/k_{dZ}): $(E/Z)_{\text{pss}} = (k_{qZ}/k_{qE})(k_{dE}/k_{dZ})$.¹⁶ Since the decay ratio k_{dE}/k_{dZ} should be independent of the sensitizer E_{T} , as was the case with cyclooctene,¹⁶ the observed variation in $(E/Z)_{\text{pss}}$ is attributable to change in the quenching ratio k_{qZ}/k_{qE} . The quite similar $(E/Z)_{\text{pss}}$ ratios for 1-methyl- and unsubstituted cyclooctenes over the entire E_{T} range examined clearly indicate that, in spite of the increased strain in the (*E*)-isomer and the lowered excited-state energy, the excitation and decay ratios are not seriously influenced by methyl substitution in cyclooctene. Another important conclusion is that the increased steric hindrance does not play any crucial role in the triplet sensitization, since no drastic changes in $(E/Z)_{\text{pss}}$ is found even in the triplet sensitizations of 1-methyl- and unsubstituted cyclooctenes with highly bulky *p*-di-*tert*-butylbenzene.

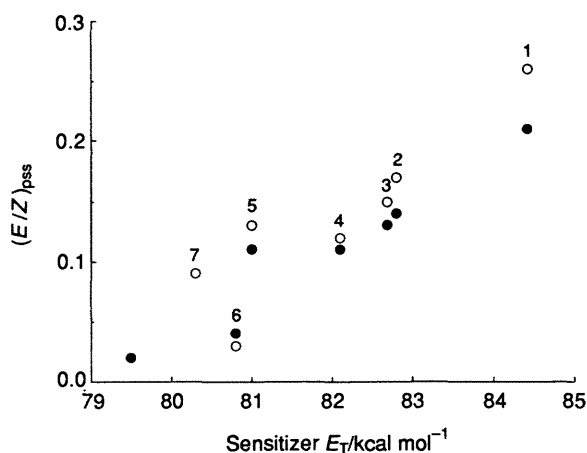
Singlet Sensitization.—It has been demonstrated that a wide variety of (poly)alkyl benzene(poly)carboxylates function as efficient singlet sensitizers for the geometrical photoisomerization of simple alkenes *via* exciplex intermediates.^{15,22,23} In the present study, the singlet-sensitized photoisomerization

Table 2 Photostationary state E/Z ratio, $(E/Z)_{\text{pss}}$, of 1-methylcyclooctene at various substrate concentrations upon triplet photosensitization with aromatic hydrocarbons in pentane at 25 °C

Sensitizer (0.1 mol dm ⁻³)			[1-Methylcyclooctene]/mmol dm ⁻³				
No.	Compound	E_T /kJ mol ⁻¹ (kcal mol ⁻¹)	30	10	2	0.5	0.2
1	Benzene	353 (84.3)	0.05		0.16	0.23	0.26
2	Toluene	346 (82.8)		0.13	0.17	0.17	
3	Cumene	346 (82.7)			0.16	0.15	
4	<i>o</i> -Xylene	344 (82.1)			0.12	0.12	
5	<i>m</i> -Xylene	339 (81.0)			0.13	0.13	
6	<i>p</i> -Di- <i>tert</i> -butylbenzene	338 (80.8)			0.04	0.03	
7	<i>p</i> -Xylene	336 (80.3)			0.10	0.09	

Table 3 Photostationary state E/Z ratios, $(E/Z)_{\text{pss}}$, of cyclooctene and 1-methylcyclooctene upon singlet photosensitization with (poly)methyl benzene(poly)carboxylates in pentane at 25 °C

Sensitizer	Cyclooctene	1-Methylcyclooctene
Benzoate	0.25	0.24
Phthalate	0.06	0.01
Terephthalate	0.29	0.06
1,2,4,5-Benzenetetracarboxylate	0.10	0.01

**Fig. 5** Photostationary state E/Z ratios, $(E/Z)_{\text{pss}}$, as a function of triplet energy (E_T) of sensitizer upon triplet photosensitized isomerization of 1-methylcyclooctene (○) and cyclooctene (●) with aromatic hydrocarbons; numbers on the plot refer to the sensitizer numbers in Table 2

of 1-methylcyclooctene (30 mmol dm⁻³) was performed by using methyl benzoate, phthalate, terephthalate, and 1,2,4,5-benzenetetracarboxylate as sensitizers to give the geometrical isomerization as the sole photoreaction observed. The photostationary state E/Z ratios, shown in Table 3, were similarly determined for these benzene(poly)carboxylates.

In sharp contrast to the triplet sensitization described above, the singlet sensitization of 1-methylcyclooctene was shown to be much more sensitive to substitution in the sensitizer as compared with the cyclooctene case. As can be seen from Table 3, less congested benzoate gives comparable $(E/Z)_{\text{pss}}$ ratios of ca. 0.25 for both 1-methyl- and unsubstituted cyclooctenes, whereas the $(E/Z)_{\text{pss}}$ ratio for 1-methylcyclooctene is dramatically reduced, by a factor of 5–10, with increasing numbers of methoxycarbonyl groups in sensitizer, affording $(E/Z)_{\text{pss}}$ ratios as low as 0.01–0.06 for the benzenepolycarboxylates. According to the singlet sensitization mechanism shown above and the substitution-insensitive decay ratios ($k_{\text{dE}}/k_{\text{dZ}} = 0.76$ – 0.79) reported for unsubstituted cyclooctene,¹⁵ we infer that the drastically reduced $(E/Z)_{\text{pss}}$ ratio observed for 1-methylcyclo-

octene should not be attributed to a decrease in the decay ratio ($k_{\text{dE}}/k_{\text{dZ}}$) from ¹p, but is ascribable to the decreased excitation ratio ($k_{\text{qZ}}/k_{\text{qE}}$). Since no such significant difference in $(E/Z)_{\text{pss}}$ or $k_{\text{qZ}}/k_{\text{qE}}$ is seen in the triplet sensitization, the much reduced $(E/Z)_{\text{pss}}$ ratios for 1-methylcyclooctene in the singlet sensitization are probably caused by the increased steric hindrance within the singlet exciplex, especially for (*Z*)-1-methylcyclooctene rather than the (*E*)-isomer. This seems reasonable, since the (*Z*)-isomer, possessing a lower ionization potential,²⁹ requires a closer distance to attain efficient energy transfer within an exciplex intermediate with charge-transfer character and must be more sensitive to the steric hindrance.

These low $(E/Z)_{\text{pss}}$ ratios upon singlet sensitization with benzenepolycarboxylates are not advantageous from the synthetic point of view. However, the singlet-sensitized photoisomerization with benzoate can be used as the only practical one-step route to the highly constrained (*E*)-1-methylcyclooctene. As described in the Experimental section, the preparative-scale irradiation of (*Z*)-isomer (0.2 mol dm⁻³) in the presence of methyl benzoate (33 mmol dm⁻³) affords an apparent photostationary-state mixture of $E/Z = 0.20$, from which the (*E*)-isomer of >99% purity is isolated in 7% yield through the modified silver nitrate extraction technique. In spite of the increased strain energy, the isolated (*E*)-1-methylcyclooctene is as stable as (*E*)-cyclooctene and can be stored for several months in a freezer at -30 °C.

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