

SOME NEW EXAMPLES OF "trans" CYCLOHEXENES: PROPERTIES CHARACTERISTIC OF THESE SPECIES

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Summary

The spectroscopic and kinetic properties of five new "trans" cyclohexene derivatives have been determined and compared with the properties of the three previously reported "trans" cyclohexenes. These properties appear to be remarkably constant for the whole series of investigated compounds, except for a few exceptions which can be easily explained. Therefore we propose the following properties as characteristic of a "trans" cyclohexene derivative. The maximum of the UV absorption band is shifted to the red by about $15\,000\text{ cm}^{-1}$ with respect to the maximum of the intense $\pi\pi^*$ absorption band of the cis form (at least when this band originates from the second $\pi\pi^*$ transition). The activation energy for the thermal "trans" \rightarrow cis isomerization is about 42 kJ mol^{-1} and the corresponding pre-exponential factor is in the range $10^{12} - 10^{13}\text{ s}^{-1}$. If markedly different values are found for these parameters, another reaction is probably competing with the thermal isomerization. The presence of oxygen has little or no influence on the lifetime of the "trans" species but, when the "trans" species is populated via the perpendicular triplet, the amount of "trans" isomer is greatly reduced since the yield of conversion of the triplet into the "trans" form is four to five times smaller for the perpendicular triplet interacting with oxygen than for the same triplet species in the absence of oxygen. This effect is amplified when a large proportion of the triplets are planar since the quenching of the planar triplet gives exclusively the cis ground state.

1. Introduction

Some years ago, we reported the first spectroscopic observation of a "trans" cyclohexene, the "trans" isomer of 1-phenylcyclohexene (1-PC6) [1, 2], rapidly followed by the "trans" 1-acetylcyclohexene (1-AC6) [3]. Recently we observed the "trans" form of 1,1'-bicyclohexenyl (1,1'-BC6) [4]. The absorption spectrum of the "trans" isomer of these three very different compounds was, in each case, shifted to the red by about $15\,000\text{ cm}^{-1}$ with respect to the intense allowed $\pi\pi^*$ transition of the initial cis

isomer (considering the absorption maxima). The lifetimes of these "trans" species were about 10, 15 and 0.8 μs , at room temperature, and were found to be strongly temperature dependent because of the existence of an activation energy barrier of approximately 33 kJ mol^{-1} on the path of the "trans" \rightarrow cis isomerization. Recently, Caldwell has reported an unusually large isotope effect on the lifetime of the "trans" 1-PC6 which is increased by a factor of 2 when the vinylic hydrogen atom is exchanged for a deuterium atom [5] but we don't know whether this is due to a change in the activation energy or a change in the frequency factor.

We now report the observation of five new "trans" arylcyclohexenes, their absorption spectra and the temperature dependence of their lifetimes. The spectroscopic and kinetic properties of the whole series of "trans" cyclohexenes are compared and the differences which appear in a few cases are explained.

2. Experimental details

The excitation was provided by a mode-locked Nd-YAG laser (200 ps pulses) frequency tripled (355 nm) or quadrupled (266 nm), in a crossed beams arrangement as described previously [6]. The analysing light source was a 75 W xenon arc operated at 15 V by a stabilized power supply for the measurement of lifetimes longer than 2 μs ($R_L = 1 \text{ k}\Omega$, $\tau_r = 200 \text{ ns}$) or pulsed at 90 V during 1 ms when the measured lifetimes were shorter than 5 μs ($R_L = 50 \Omega$, $\tau_r = 5 \text{ ns}$).

In most cases the "trans" ground state was populated via the triplet, using xanthone excited at 355 nm as a sensitizer and benzene as the solvent

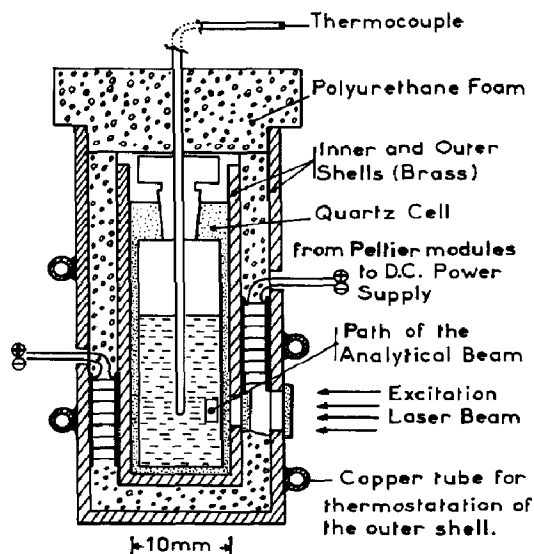
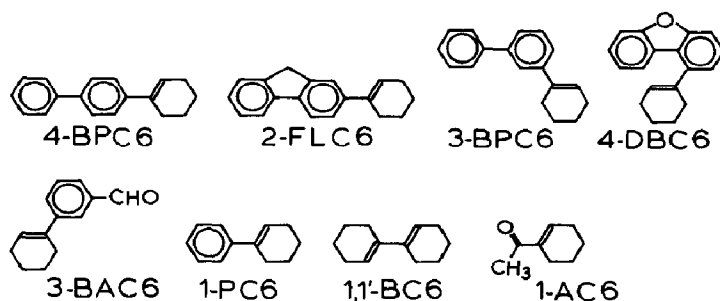


Fig. 1. Experimental system used for varying and measuring the temperature of the sample.

with a concentration of cyclohexene derivative in the range 0.005 - 0.025 M. In a few cases, the cyclohexenyl compound was directly excited at 266 nm in cyclohexane or acetonitrile.

The temperature of the solution could be varied in the range 273 - 353 K by surrounding the 10 mm × 10 mm spectroscopic cell with four Peltier modules (Melchor Frigichips) and it was monitored by immersing a stainless steel clad thermocouple in the solution in the vicinity of the path of the analysing beam (see Fig. 1). The solutions were flushed with N₂ or, when needed, with commercial mixtures of N₂-O₂ containing 10 or 50 vol.% O₂.

The arylcyclohexenes were prepared from the aryl bromide and cyclohexanone by Grignard reaction followed by dehydration of the resulting alcohol. The compounds investigated in this study have the following structures:



3. Results

The absorption spectra of the five new aryl "trans" cyclohexenes and of the "trans" 1,1'-bicyclohexenyl are given in Fig. 2. In each case the spectrum consists of a broad structureless band with a full width at half-maximum of about 5000 cm⁻¹. The wavelengths of maximum absorption of the cis and trans isomers and the corresponding red shifts $\Delta\nu$ are listed in Table 1. The

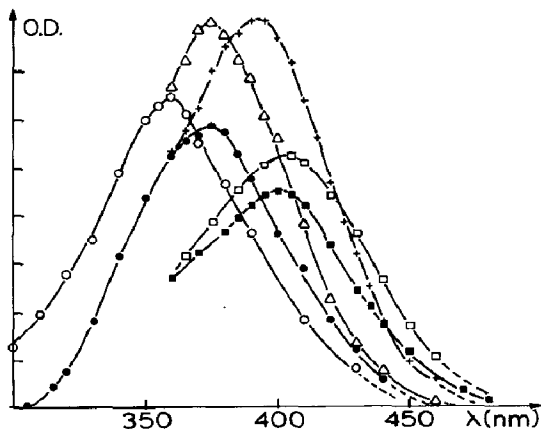


Fig. 2. Absorption spectra of the "trans" species of the studied cyclohexene derivatives: ●, 3-BAC6; ▲, 3-BPC6; +, 4-BPC6; □, 4-DBC6; ■, 2-FLC6; ○, 1,1'-BC6.

TABLE 1
Spectroscopic data

	3-BAC6	3-BPC6	4-DBC6	4-BPC6	2-FLC6	1-PC6	1-AC6	1,1-BC6
$\lambda_{\max}(\text{cis})$ (nm)	239	244	255	276	285	248	227	238
$\lambda_{\max}(\text{trans})$ (nm)	375	375	405	392	400	385 ^a	345 ^b	360 ^c
$\Delta\nu$ (cm ⁻¹)	15170	14320	14500	10720	10090	14800	15070	14200
A_0 ($\times 10^{12}$ s ⁻¹)	3.0	7.8	2.4	7.2	6.6	7.4	0.9	2.1 1.2 ^c
ΔE_a (kJ mol ⁻¹)	41.0	44.2	42.04	41.8	41.2	44.5 31.3 ^d	42.7	35.6 34.0 ^c

^aFrom ref. 1.

^bFrom ref. 2.

^cFrom ref. 3.

^dFrom ref. 4.

temperature dependence of the lifetime was studied according to the Arrhenius formalism, by plotting $\ln(1/\tau)$ vs. $1/T$. These plots are shown in Fig. 3 and the resulting pre-exponential factors A_0 and activation energies ΔE_a are listed in Table 1. In each case, the value of A_0 is in the range $10^{12} - 10^{13} \text{ s}^{-1}$ and ΔE_a is between 41 and 44 kJ mol^{-1} . These data are significantly different from those found previously for 1-PC6 from a study over the temperature range 203 - 303 K. This prompted us to re-examine 1-PC6 and also 1-AC6 since the temperature dependence of the "trans" form of the latter compound was not measured in our previous work [3]. The plots of $\ln(1/\tau)$ vs. $1/T$ are shown in Fig. 4 and the values of A_0 and ΔE_a (listed in Table 1) are in fair agreement with those determined for the five new aryl "trans" cyclohexenes. The lifetimes of the "trans" cyclohexenes, which are ground state species, are not very sensitive to oxygen. However, in some cases, we noticed a slight reduction in the lifetime, probably because of reaction (addition?). For instance, the plot of $1/\tau$ vs. $[\text{O}_2]$ gives a (reaction) rate constant equal to $4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 3-BPC6 and $9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 2-FLC6. The main effect of the presence of O_2 is a strong reduction in the amount of the "trans" isomer when this species is produced by the triplet pathway, an effect which has been already found for 1-PC6 and 1-phenylcycloheptene but which has not been observed for acyclic arylethylenes [7]. Of course, oxygen competes with the arylcyclohexene to quench the triplet of the xanthone sensitizer but, on account of the high concentrations of arylcyclohexene, this effect is small and can be quantitatively evaluated. The ratios of the absorption of the "trans" species in the presence to that in the absence of oxygen, OD/OD_0 , given in Table 2 have been corrected for this effect.

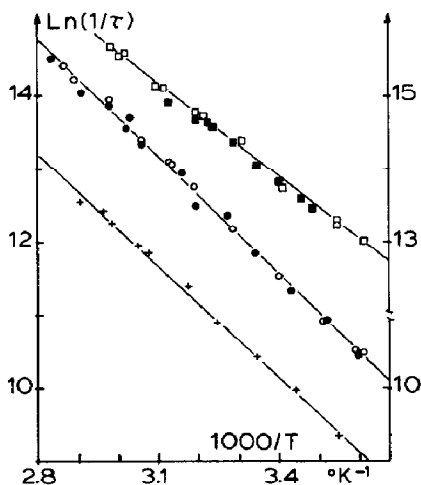
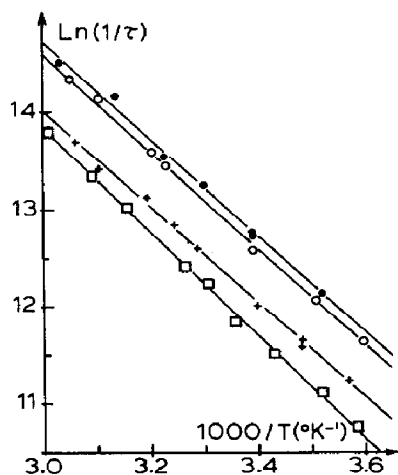


Fig. 3. Arrhenius plots of the reciprocal lifetime of the "trans" species of the following compounds (in C_6H_6): +, 3-BAC6; \square , 3-BPC6; \circ , 4-PBC6; \bullet , 2-FLC6.

Fig. 4. Arrhenius plots of the reciprocal lifetime of the "trans" species of 1-PC6 in benzene (\circ) or cyclohexane (\bullet), 1-AC6 in acetonitrile (+) and 1,1'-BC6 in benzene (\square) or acetonitrile (\blacksquare). The last set of points is taken from previous work [4].

TABLE 2

	$\phi/\phi_0 = OD/OD_0$				τ_0 (ns) ([O ₂] = 0 vol.%)	k_Q (M ⁻¹ s ⁻¹) ([O ₂] = 0 · 100 vol.%)
	[O ₂] = 10 vol.%	[O ₂] = 21 vol.%	[O ₂] = 50 vol.%	[O ₂] = 100 vol.%		
1-PC6	0.76	0.61	0.45	0.36	65	8 × 10 ⁹
3-BPC6	0.74	0.60	0.43	0.34	70	8 × 10 ⁹
4-BPC6	0.58	0.42	0.28	0.21	180	5 × 10 ⁹
2-FLC6	0.59	0.39	0.26	(0.77) ^a	220	4.5 × 10 ⁹

The concentration of O₂ in benzene flushed with pure O₂ under 1 atm pressure (100% O₂) is assumed to be 0.01 M. The values of τ/τ_0 used in the plots of Fig. 7 are calculated from $\tau/\tau_0 = 1/(1 + \tau_0 k_Q [O_2])$.

^aValue obtained for a very low concentration of oxygen (about 4 vol.% as deduced from τ , τ_0 and k_Q).

4. Discussion

Table 1 indicates that the following are the general properties of the "trans" cyclohexenes: (i) the maximum of the absorption band is red shifted by $14\,700 \pm 500\text{ cm}^{-1}$ with respect to the maximum of the intense $\pi\pi^*$ band of the cis isomer; (ii) the lifetime is a few microseconds at room temperature and is determined, in the absence of reaction, by the rate of the thermal "trans" → cis isomerization; (iii) this rate is strongly temperature dependent with an activation energy close to 42 kJ mol⁻¹ and a pre-exponential factor in the range $(1 - 8) \times 10^{12}\text{ s}^{-1}$. These "rules" suffer a few exceptions which will be discussed and rationalized.

For 4-BPC6 and 2-FLC6 the red shift is about $10\,000\text{ cm}^{-1}$, far from the standard value. This is explained by a change in the nature of the absorption band of the cis isomer used as the reference for measuring $\Delta\nu$. For 1-PC6, 3-PBC6 and 1,1'-BC6, the absorption band used as the reference is the second $\pi\pi^*$ absorption band. The first $\pi\pi^*$ transition is forbidden, with extinction coefficients in the range $10^2 - 10^3\text{ M}^{-1}\text{ cm}^{-1}$, and appears as a small shoulder when the absorption spectra are plotted on a logarithmic scale (Fig. 5) or in the fluorescence excitation spectrum shown in Fig. 6. The situation is quite different for 4-PBC6: the absorption spectrum shows a single broad band without any shoulder that could be assigned to a forbidden $S_0 \rightarrow S_1$ transition, the compound is highly fluorescent and the fluorescence lifetime is short. Therefore the first $\pi\pi^*$ transition is allowed and the second $\pi\pi^*$ band, which should be used as the reference, is hidden and probably mixed with the strong $S_0 \rightarrow S_1$ absorption. This change in the character of the two first $\pi\pi^*$ transitions of 3-PBC6 and 4-PBC6 is supported by the similarity of the spectroscopic properties (absorption and fluorescence spectra and fluorescence lifetimes) of these compounds to those of *m*-terphenyl and *p*-terphenyl, the former being very close to those of biphenyl. Even though the non-planarity of these molecules and their changes in geometry between

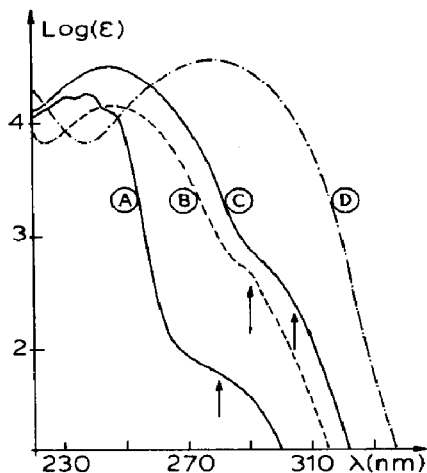


Fig. 5. Absorption spectra on a logarithmic scale of the stable form of 1,1'-BC6 (curve A), 1-PC6 (curve B), 3-PBC6 (curve C) and 4-PBC6 (curve D) in C_6H_{12} . The arrows indicate the approximate position of the first forbidden transition, which is not observed in the case of 4-BPC6.

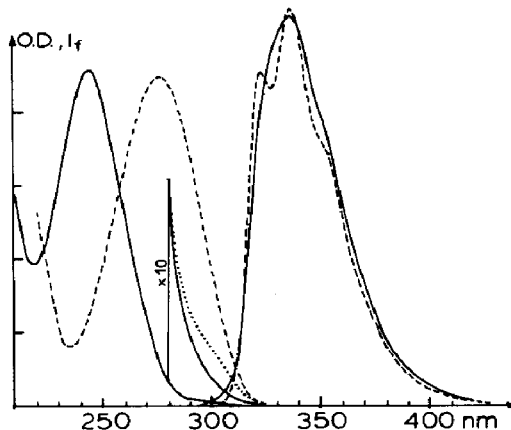


Fig. 6. Absorption and fluorescence spectra of 3-PBC6 (full lines) and 4-PBC6 (broken lines). These spectra are nearly identical in shape and position with those of *m*- and *p*-terphenyl (see for instance ref. 8). A small part of the fluorescence excitation spectrum of 3-PBC6 is also shown (. . .).

ground and excited states prevent precise energy level calculations from being carried out, theoretical calculations agree with experimental observations to give an inversion of the energy ordering of the first allowed and forbidden $\pi\pi^*$ transitions when going from biphenyl to *p*-terphenyl [9, 10], whereas these two transitions would be nearly isoenergetic in 4-vinylbiphenyl [11].

The same explanation may be used in the case of 2-FLC6, where the absorption band at 285 nm is related to the $S_0 \rightarrow S_1$ transition whereas the $S_0 \rightarrow S_1$ transition, which would be relevant for the calculation of $\Delta\nu$, is not observed.

For 1-PC6 and 1,1'-BC6 the values previously determined for ΔE_a were significantly lower than 42 kJ mol^{-1} . In fact the value redetermined in the present study for 1-PC6 is very close to the "standard" value. The previous evaluation ($\Delta E_a \approx 30 \text{ kJ mol}^{-1}$) was made in methanol between 203 and 303 K and the plot of $\ln(1/\tau)$ vs. $1/T$ was clearly curved for $T < 223 \text{ K}$. This was interpreted by assuming that the addition reactions of the "trans" isomer to the cis isomer and to methanol have a low activation energy and compete with the "trans" \rightarrow cis isomerization. This assumption was confirmed by analysis of the products formed under irradiation at 200 K [2]. ΔE_a was therefore determined by considering only the temperature range 233 - 303 K but, even so, the measured slope was probably affected by the addition processes. The present value is much more reliable since we chose non-reactive solvents, a "high" temperature range (277 - 351 K) and low concentrations

of 1-PC6 (about 0.01 M for the sensitized irradiation in benzene and below 0.001 M for the direct irradiation in cyclohexane).

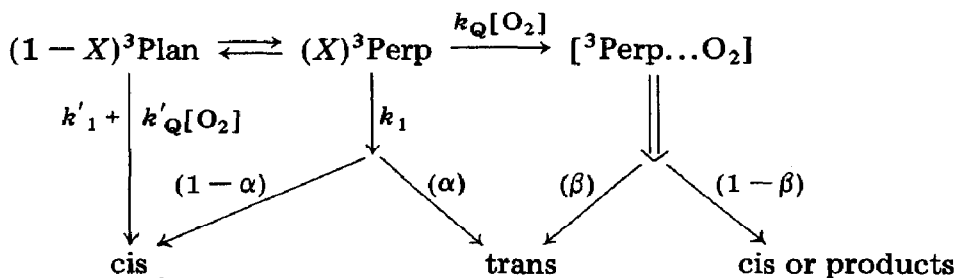
The temperature dependence of the lifetime of the "trans" 1,1'-BC6 was also redetermined in benzene. The results are fairly close to those obtained previously in acetonitrile [4] and least-squares analysis of the data obtained in both solvents (*cf.* Fig. 4) gives $\Delta E_a = 35.6 \text{ kJ mol}^{-1}$ and $A_0 = 2.1 \times 10^{12} \text{ s}^{-1}$. Again, the low value of ΔE_a may be explained by the "trans" species undergoing a reaction (the formation of a cyclobutene derivative) [4] which probably has a lower activation energy than the thermal isomerization, making the measured ΔE_a lower than expected and the lifetime of the "trans" species unusually short. This process cannot be minimized by changing the experimental conditions since it is an intramolecular reaction. Thus, the activation energy for the thermal "trans" \rightarrow cis isomerization of cyclohexenes seems to be about 42 kJ mol^{-1} in all cases: if a markedly different value is measured, this indicates that another reaction is most probably competing with the isomerization.

The pre-exponential factor A_0 is in the range $(2 - 8) \times 10^{12} \text{ s}^{-1}$ with a mean value equal to $5.2 \times 10^{12} \text{ s}^{-1}$ if 1-AC6 is not taken into account. This is very close to the frequency factor, $k_0T = 6.45 \times 10^{12} \text{ s}^{-1}$ at 310 K, which appears in the equation given by transition state theory:

$$k = k_0T \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta E^\ddagger}{RT}\right)$$

This means that the entropy term ΔS^\ddagger must be very small and, indeed, the plots of $\ln(1/\tau) - \ln T$ *vs.* $1/T$ give ΔS^\ddagger in the range -1 to -2 cal K^{-1} for most of the compounds and ΔE^\ddagger which are about 2.1 kJ mol^{-1} lower than the corresponding ΔE_a . The small value of ΔS^\ddagger indicates that there is little difference between the "degree of order" of the transition state and that of the "trans" species. Since the transition state (the ground state with the double bond twisted by 90°) is well defined in this reaction, the structure of the "trans" form must be well defined too, the methylene chain being stretched and fixed in the conformation which allows the largest twist for the double bond. In contrast, the geometry of the "trans" cycloheptene, a much less strained compound, is probably more flexible since $\Delta S^\ddagger \approx -9 \text{ cal K}^{-1}$ has been reported for this compound [12].

Consider the effect of oxygen on the yield of formation of the "trans" cyclohexenes from the triplet state. This effect may be explained by assuming that the perpendicular triplet precursor of the "trans" isomer gives a complex with oxygen and that, in the case of 1-PC6 where the perpendicular geometry is the only metastable conformation of the lowest triplet, the yield of formation of the "trans" species from this complex is four times smaller than it is from the uncomplexed triplet [7]. We wondered whether the same decrease of a factor of 4 would be observed with other compounds and what would happen when the planar and perpendicular geometries of the triplet coexist in equilibrium. The system can be represented by the following scheme:



where k_1 and k'_1 are $1.54 \times 10^7 \text{ s}^{-1}$ and 10^5 s^{-1} and k_Q and k'_Q are $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively. (The values $k'_1 \lesssim 10^5 \text{ s}^{-1}$ and $k'_Q = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ are those usually found for a high energy triplet state; $k_1 = 1.54 \times 10^7 \text{ s}^{-1}$ and $k_Q = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ are the values measured for the perpendicular triplet of 1-phenylcyclohexene.) In the absence of oxygen, the yield of conversion of the triplet into the "trans" form is

$$\phi_0 = \alpha k_1 X \tau_0$$

with

$$\frac{1}{\tau_0} = k_1 X + k'_1 (1 - X)$$

Since $k_1 \gg k'_1$ this gives

$$\phi_0 \approx \alpha$$

$$\frac{1}{\tau_0} \approx k_1 X \quad (1)$$

as long as $X \geq 0.1$. In the presence of oxygen, the yield becomes

$$\phi = (\alpha k_1 X + \beta X k_Q [\text{O}_2]) \tau$$

with

$$\frac{1}{\tau} = X(k_1 + k_Q [\text{O}_2]) + (1 - X)k'_Q [\text{O}_2] \quad (2)$$

From eqns. (1) and (2)

$$\frac{\phi}{\phi_0} \frac{\tau_0}{\tau} = 1 + \frac{\beta}{\alpha} \frac{k_Q}{k_1} [\text{O}_2] \quad (3)$$

or, with $m = k_Q/k'_Q$ and $A = (\beta/\alpha)\{1 + (m - 1)X\}$

$$\frac{\phi}{\phi_0} = A + (1 - A) \frac{\tau}{\tau_0} \quad (4)$$

The four sets of points obtained by plotting the values given in Table 2 according to eqn. (3) give straight lines with slopes respectively equal to 123 M^{-1} , 125 M^{-1} , 112 M^{-1} and 110 M^{-1} which yield values of β/α between 0.21 and 0.24. The whole set of data may be fitted by a single straight line ($r^2 = 0.993$) with a slope equal to 120 M^{-1} which gives $\beta/\alpha = 0.23$ (see Fig. 7(a)).

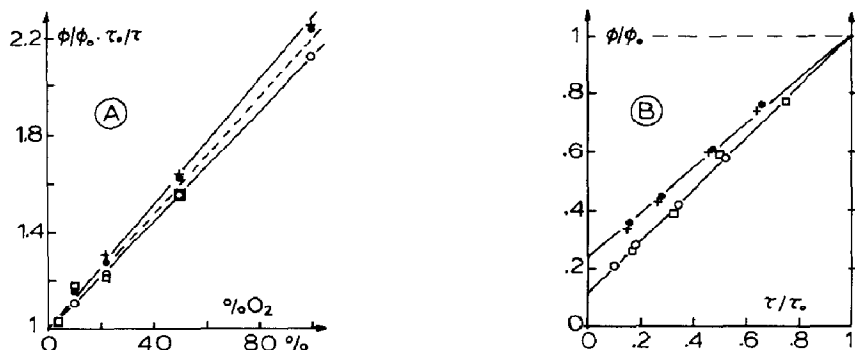


Fig. 7. Effect of oxygen on the yield of conversion of the triplet into the "trans" species. Plots of (a) $(\phi/\phi_0)(\tau_0/\tau)$ vs. $[O_2]$ according to eqn. (3) and of (b) ϕ/ϕ_0 vs. τ/τ_0 according to eqn. (4). The values of (ϕ/ϕ_0) are taken from Table 2 and those of (τ/τ_0) are calculated from the values of τ_0 and k_Q given in the table: ●, 1-PC6; +, 3-PBC6; ○, 4-BPC6; □, 2-FLC6.

The proportions of planar and perpendicular triplets do not appear in the previous treatment but they do in the plot of ϕ/ϕ_0 vs. τ/τ_0 according to eqn. (4). The intercepts of the straight lines in Fig. 7(b) give $A = 0.24$ for 1-PC6 and 3-BPC6 and $A = 0.12$ for 4-BPC6 and 2-FLC6. The triplet of the first two compounds is essentially perpendicular as shown by its short lifetime; therefore $X \approx 1$ and $\beta/\alpha = 0.24$. For the other two the expression $1/X = k_1\tau_0$ gives $X = 0.30$ and $X = 0.36$ and, with $m = 8/3$ and $A = 0.12$, one gets $\beta/\alpha = 0.225$ and $\beta/\alpha = 0.2$ respectively. In this case the decrease in the amount of "trans" form is amplified by the fact that the quenching by oxygen of the triplets which have a planar geometry gives exclusively the cis ground state.

Thus, for the four investigated compounds, the yield of production of the "trans" species from the complex (${}^3\text{Perp}\dots\text{O}_2$) is four to five times smaller than from the uncomplexed perpendicular triplet. Since the compounds studied are very different in character, the triplets of two being fully or mainly perpendicular whereas the other two are nearly planar, oxygen probably has a similar effect on any cyclohexenyl derivative.

5. Conclusions

The spectroscopic and kinetic properties of eight "trans" cyclohexene derivatives have been compared, and it appears that these properties are remarkably constant: (i) the absorption spectrum is a broad structureless band, red shifted by about $15\,000\text{ cm}^{-1}$ with respect to the maximum of the intense second $\pi\pi^*$ absorption band of the stable cis form; (ii) the activation energy for the thermal "trans" \rightarrow cis isomerization is around 42 kJ mol^{-1} and the frequency factor for this process is in the range $10^{12} - 10^{13}\text{ s}^{-1}$, indicative of a very low entropy change between the "trans" and the perpendicular ground state; (iii) the yield of conversion of the perpendicular triplet to the

“trans” ground state is reduced by a factor of 4 - 5 when the triplet interacts with oxygen. The resulting decrease in the amount of the “trans” isomer produced may be amplified by the quenching of the planar triplet since an appreciable number of the triplets are planar. The few exceptions to points (i) and (ii) can easily be rationalized.

Acknowledgments

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