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Ab initio Infrared Spectra and Inversion Barriers of Dibenzo [*a,c*]cycloocta-5,8-diones

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Ab initio calculations are carried out for stereo-specific inversions of 6XX´-7YY´-dibenzo[*a,c*]cyclooctadiene-5,8-dione, **1**: X=X´=Y=Y´=H; **2**: X=X´=Y=Y´=CH_3; **3**: X=Y= H, X´=Y´=CH_3; **4**$_{cis}$: Y´=H, X´=Y=CH_3; **4**$_{trans}$: X´=CH_3, Y´=Y=H; **5**$_{cis}$: X=Y´=H, X´=Y= *i*-pr and **5**$_{trans}$: X=X´= *i*-pr, Y´=Y=H. Inversion energy barriers of **1-5**, to their corresponding conformers **1'-5'**, are determined *via ab initio* calculations. These are preformed at HF/6-31G* and MP2/6-31+G* levels of theory, using Gaussian 98 system of programs. The order of energy barriers/(kcal/mol) found for the inversions is: $\mathbf{3} \rightleftharpoons \mathbf{3'}$ (34.00) > $\mathbf{2} \rightleftharpoons \mathbf{2'}$ (28.05) > $\mathbf{5}_{cis} \rightleftharpoons \mathbf{5'}_{cis}$ (27.21) > $\mathbf{5}_{trans} \rightleftharpoons \mathbf{5'}_{trans}$ (24.75) > $\mathbf{4}_{cis} \rightleftharpoons \mathbf{4'}_{cis}$ (22.35) > $\mathbf{4}_{trans} \rightleftharpoons \mathbf{4'}_{trans}$ (21.62) > $\mathbf{1} \rightleftharpoons \mathbf{1'}$ (19.47). Enantiomeric conformers **4**$_{cis}$ and **4´**$_{cis}$ have the same energy. Similarly, **5**$_{cis}$ and **5´**$_{cis}$, which are mirror images, have the same energy. Diastereomeric conformers **4**$_{trans}$ and **4´**$_{trans}$ are at different energies. So are **5**$_{trans}$ and **5´**$_{trans}$. Important factor that cause to observing two absorbance for each of *cis* and an absorbance for each of **4**$_{trans}$ and **4´**$_{trans}$; **5**$_{trans}$ and **5´**$_{trans}$ is relative position of carbonyl group and closer benzene ring.

Key Words: Dibenzo [*a,c*]cycloocta-5,8-diones, *ab initio* calculations, HF and DFT methods, Dynamic NMR, Steric effects.

INTRODUCTION

Now-a-days, *ab initio* calculations are used to reach for unreachable data, beyond experimental limits[1-8]. Studies related to strain, conformations and transannular interactions of cyclooctanes appear of considerable interest[9-13]. The reactivity and stereoselectivity exhibited by eight-membered rings are customarily investigated *via* dynamic NMR spectra[14]. The eight-membered rings are important moieties of numerous natural products, including terpinoids[15,16]. Many of them exhibit exceptional, broad

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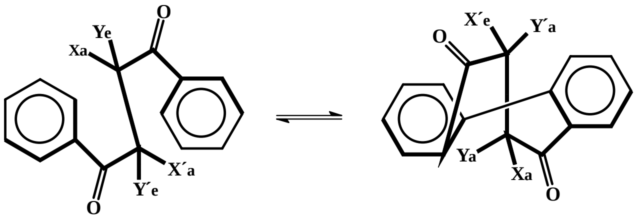
ranging biological activities. A vivid example is the diterpine, paclitaxel which is used as a clinical anticancer drug[17-20].

This work focuses on inversion barriers of dibenzo [*a*,*c*] cycloocta-5,8-diones(**1-5** to **1'-5'**). Treatment of substituted 2, 2-*bis*[1-oxa-2-bromoalkyl]biphenyls with zinc-copper (in DMSO), in the presence of sodium iodide and sodium bicarbonate, results in the formation of derivatives of **1-5** (**Scheme-I**). Dynamic nuclear magnetic resonance (D NMR) studies on geometrical isomers of **4** have already been reported[14].

In present studies *ab initio* calculations in order to find data on inversions of **1**, **2**, **3** and **5** has been employed. Our data complete and confirm the experimental findings reported on **4**. Thermodynamic data are also obtained for $\mathbf{1} \rightleftharpoons \mathbf{1'}$, $\mathbf{2} \rightleftharpoons \mathbf{2'}$, $\mathbf{3} \rightleftharpoons \mathbf{3'}$, $\mathbf{4}_{cis} \rightleftharpoons \mathbf{4'}_{cis}$, $\mathbf{4}_{\text{trans}} \rightleftharpoons \mathbf{4'}_{\text{trans}}$, $\mathbf{5}_{cis} \rightleftharpoons \mathbf{5'}_{cis}$ and $\mathbf{5}_{\text{trans}} \rightleftharpoons \mathbf{5'}_{\text{trans}}$ equilibriums (**Scheme-I**).



X_a	Y_e	X'_a	Y'_e	E_a(kcal/mol)	X_a	Y_e	X'_a	Y'_e
H	H	H	H	$1 \xrightleftharpoons{19.47} 1'$	H	H	H	H
CH_3	CH_3	CH_3	CH_3	$2 \xrightleftharpoons{28.05} 2'$	CH_3	CH_3	CH_3	CH_3
H	H	CH_3	CH_3	$3 \xrightleftharpoons{34.00} 3'$	H	H	CH_3	CH_3
H	CH_3	CH_3	H	$4_{\text{cis}} \xrightleftharpoons{22.35} 4'_{\text{cis}}$	H	CH_3	CH_3	H
CH_3	H	CH_3	H	$4_{\text{trans}} \xrightleftharpoons{21.63\ (17.87)} 4'_{\text{trans}}$	CH_3	H	CH_3	H
H	*i*-Pr	*i*-Pr	H	$5_{\text{cis}} \xrightleftharpoons{27.31} 5'_{\text{cis}}$	H	*i*-Pr	*i*-Pr	H
i-Pr	H	*i*-Pr	H	$5_{\text{trans}} \xrightleftharpoons{24.75\ (24.62)} 5'_{\text{trans}}$	*i*-Pr	H	*i*-Pr	H

Scheme-I: Inversion energy barrier (E_a) between dibenzo [*a*,*c*]cycloocta-5,8-dione derivatives, **1-5**, and their corresponding conformers, **1´-5´**. Values shown in parentheses indicate E_a associated with $\mathbf{4'}_{trans}$ and $\mathbf{5'}_{trans}$ to their corresponding $\mathbf{4}_{trans}$ and $\mathbf{5}_{trans}$, respectively

Computational methods

Calculations are preformed using the Gaussian 98 system of programs[21]. The geometrical structures, corresponding to the ground states and transition states are investigated at HF/STO-3G level. To assess the performance of this approach, all species are computed at higher theoretical levels. Therefore, the STO-3G outputs are used as inputs for the HF/6-31G* calculations and geometry reoptimizations are carried out using the same method. In both levels, for finding energy minima keyword: 'OPT' and transition states keyword: 'OPT (QST3)' is used. In order to confirm the nature of the stationary species and evaluate the activation energy barriers, frequency calculations (keyword: FREQ) are carried out for ground and transition states at HF, MP2 and DFT levels. Thermodynamic functions obtained through frequency calculations, are multiplied by the scaling factor. This is to account for the difference between the harmonic vibrational calculations and the anharmonic oscillations of the actual bonds. For minimum state structures, only real frequency values and for the transition states, merely single imaginary frequency value is accepted. Also reaction path are followed by IRC to confirm transition states related to the corresponding minimums[22,23].

Simulated IR spectra are created by making a script using a freqchk option of Gaussian 98. This option produces the B-matrix elements from calculated Cartesian coordinates. These B-matrix elements were used to convert the *ab initio* force filed in Cartesian coordinates to a force field in desired internal coordinates. These force fields were used in a mass weighted Cartesian coordinate calculation to reproduce the *ab initio* vibrational frequencies and to the determine the potential energy distribution.

RESULTS AND DISCUSSION

The goal of this research is to find inversion energy barrier (E_a), associated with dibenzo [*a,c*]cycloocta-5,8-dione derivatives, **1-5**, to their corresponding conformers **1´-5´** (**Scheme-1**). Thermodynamic data for these ring inversions are calculated *via* HF/6-31G* and MP2/6-31+G* which include: sum of electronic and thermal energies (E), sum of electronic and thermal Gibbs free energies (G), sum of electronic and thermal enthalpies (H) and zero point vibrational energy (ZPVE) for rotational ground states (G) and transition states (TS)[†] (Table-1)[24]. Changes of activation electronic energies ($\Delta E^{\#}$), Gibbs activation free energies ($\Delta G^{\#}$), enthalpies of activation ($\Delta H^{\#}$) and rate constants (k_r)[‡] are obtained by the FREQUENCY option of the Gaussian 98 program[21] (Table-2). For the sake of comparison, the available dynamic NMR experimental activation free energy data[14] are shown within parentheses in Table-2. Introducing bulky substituents at

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[†] $G = H - TS = (E + RT) - TS = [(E_0 + E_{vib} + E_{rot} + E_{trans}) + RT] - TS$, where: $E_0 = Eelec + ZPE$.

[‡] According to the transition state theory, the rate constant (k_r), is calculated as shown by the following equation:

$$k_r = \frac{k_B T}{h} K^{\#} = \frac{k_B T}{h} e - \frac{\Delta G^{\#}}{RT}$$

TABLE-1

CALCULATED HF/6-31G* DATA FOR **1-5** $\rightleftharpoons$ **1'-5'** EQUILIBRIUM SYSTEMS, SHOWING: SUM OF ELECTRONIC AND THERMAL ENERGIES (E), SUM OF ELECTRONIC AND THERMAL ENTHALPIES (H), SUM OF ELECTRONIC AND THERMAL GIBBS FREE ENERGIES (G) ALONG WITH ZERO-POINT VIBRATIONAL ENERGIES (ZPVE) AS WELL AS MP2 AND B3LYP SINGLE POINT CALCULATIONS

Equilibrium systems	Structure	E (HF)	H (HF)	G (HF)	ZPVE (HF)	Single point (MP2)	Single point (B3LYP)
1 $\rightleftharpoons$ **1´**	**1**	-762.342670	-762.341726	-762.395741	159.7921	-764.982673	-767.3602764
	TS	-762.314110	-762.313166	-762.365127	160.0901		
	1´	-762.342670	-762.341726	-762.395739	159.7924	-764.957768	-767.3602796
2 $\rightleftharpoons$ **2´**	**2**	-918.336376	-918.335432	-918.397963	235.6158	-921.654810	-924.6029507
	TS	-918.294948	-918.294004	-918.353988	236.1222		
	2´	-918.336377	-918.335433	-918.397968	235.6122	-921.654803	-924.6029557
3 $\rightleftharpoons$ **3´**	**3**	-840.3459150	-840.344970	-840.403812	197.4190	-843.322257	-845.9863200
	TS	-840.2952690	-840.294325	-840.350495	198.0325		
	3´	-840.3459150	-840.344970	-840.403812	197.4190	-843.322257	-845.9863201
$\mathbf{4}_{cis}$ $\rightleftharpoons$ $4´_{cis}$	$\mathbf{4}_{cis}$	-840.34485	-840.343906	-840.403132	197.7062	-843.319663	-845.9857406
	TS	-840.312265	-840.311321	-840.36806	198.0890		
	$\mathbf{4´}_{cis}$	-840.34485	-840.343906	-840.403132	197.7063	-843.319660	-845.9857399
$\mathbf{4}_{trans}$ $\rightleftharpoons$ $\mathbf{4´}_{trans}$	$\mathbf{4}_{trans}$	-840.34314	-840.342196	-840.401335	197.7021	-921.654810	-845.9843445
	TS	-840.316843	-840.316843	-840.37249	197.1954		
	$\mathbf{4´}_{trans}$	-840.347679	-840.347735	-840.407334	197.4591	-921.654803	-845.9892973
$\mathbf{5}_{cis}$ $\rightleftharpoons$ $\mathbf{5´}_{cis}$	$\mathbf{5}_{cis}$	-996.335663	-996.334719	-996.405132	274.1324	-999.974371	-1003.2247989
	TS	-996.296147	-996.295139	-996.363146	275.2154		
	$\mathbf{5´}_{cis}$	-996.335663	-996.334719	-996.405132	274.1324	-999.974367	-1003.2248380
$\mathbf{5}_{trans}$ $\rightleftharpoons$ $\mathbf{5´}_{trans}$	$\mathbf{5}_{trans}$	-996.334675	-996.333731	-996.403677	274.3731	-999.977063	-1003.2235849
	TS	-996.298768	-996.297744	-996.365300	275.0245		
	$\mathbf{5´}_{trans}$	-996.334380	-996.333435	-996.403879	273.7517	-999.975793	-1003.2229907

the X and Y positions renders increase of rotational barriers with an order of (E_a/kcalmol^{-1}): (**3**$\rightleftharpoons$**3'**, 34.00) > (**2**$\rightleftharpoons$**2'**, 28.05) > (**5**$_{cis}$$\rightleftharpoons$**5'**$_{cis}$, 27.21) > (**5**$_{trans}$$\rightleftharpoons$**5'**$_{trans}$, 24.75) > (**4**$_{cis}$$\rightleftharpoons$**4'**$_{cis}$, 22.35) > (**4**$_{trans}$$\rightleftharpoons$**4'**$_{trans}$, 21.62) > (**1**$\rightleftharpoons$**1'**, 19.47); (**Scheme-1**).

TABLE-2
CALCULATED HF/6-31G* DATA **1-5 1'-5'**, SHOWING: EQUILIBRIUM CONSTANTS (k_{eq}), CHANGES OF ACTIVATION ELECTRONIC ENERGIES ($\Delta E^{\#}$), ENTHALPIES OF ACTIVATION ($\Delta H^{\#}$) AND GIBBS ACTIVATION FREE ENERGIES ($\Delta G^{\#}$). THE AVAILABLE DYNAMIC NMR EXPERIMENTAL ACTIVATION FREE ENERGY DATA ARE SHOWN WITHIN BRACKETS (REF. 14)

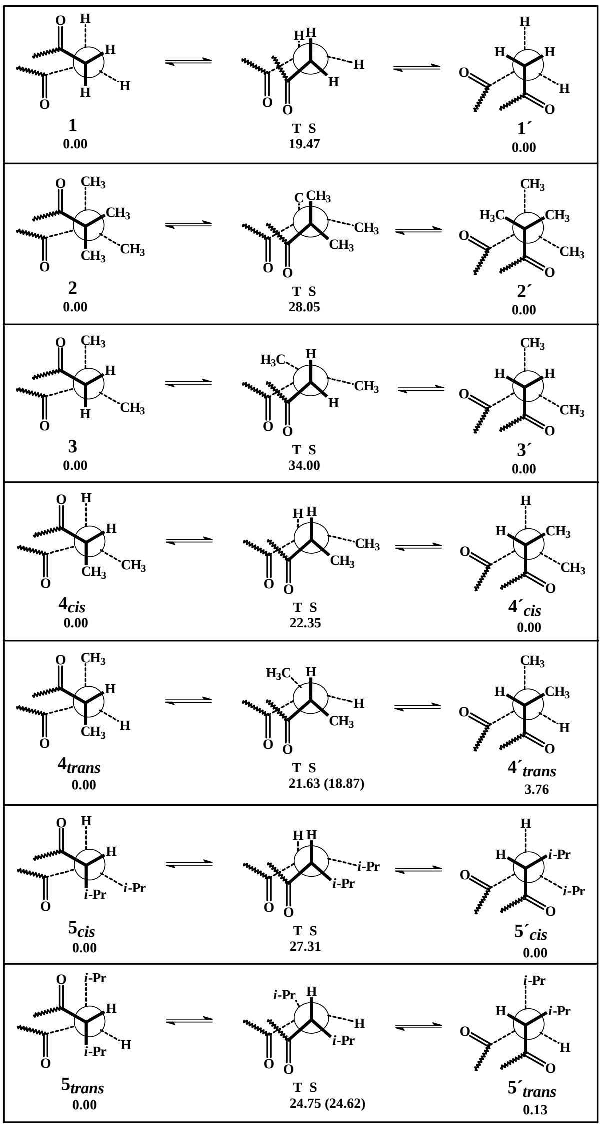
Equilibrium systems	k_{eq}	Conversions	HF/6-31G*		
			$\Delta E^{\#}$ (kcal/mol)	$\Delta H^{\#}$ (kcal/mol)	$\Delta G^{\#}$ (kcal/mol)
1 $\rightleftharpoons$ **1´**	1.0026	**1**-TS	18.19	18.19	19.47
		TS-**1´**	18.19	18.19	19.47
2 $\rightleftharpoons$ **2´**	0.9919	**2**-TS	26.45	26.45	28.05
		TS-**2´**	26.45	26.45	28.05
3 $\rightleftharpoons$ **3´**	0.9999	**3**-TS	32.33	32.33	34.00
		TS-**3´**	32.33	32.33	34.00
4$_{cis}$ $\rightleftharpoons$ 4´$_{cis}$	1.0000	**4**$_{cis}$-TS	20.79	20.79	22.35*
		TS-**4´**$_{cis}$	20.79	20.79	22.35
4$_{trans}$ $\rightleftharpoons$ **4´**$_{trans}$	0.0012	**4´**$_{trans}$-TS	19.74	19.15	21.63**
		TS-**4´**$_{trans}$	16.05	15.46	17.65
5$_{cis}$ $\rightleftharpoons$ **5´**$_{cis}$	0.9919	**5**$_{cis}$-TS	25.76	25.80	27.31
		TS-**5´**$_{cis}$	25.76	25.80	27.31
5$_{trans}$ $\rightleftharpoons$ **5´**$_{trans}$	0.3689	**5**$_{trans}$-TS	23.47	23.53	25.34
		TS-**5´**$_{trans}$	23.20	23.20	24.75

* = Ref. 18; ** = Ref. 14.

One may expect the highest energy barrier, among the set, for conversion of **2** to **2'**, which requires passing through a transition state (TS) with four eclipsing methyl groups (**Scheme-2**). Such expectation is not confirmed by our *ab initio* calculations, despite the fact that the TS involved do portray the highest steric effect. This is due to the higher potential energy associated with the gauche ground states **2** and **2'**. Hence, the highest energy barrier is anticipated for conversion of **3** to **3'** (E_a = 34 kcal/mol), due to the higher stability of the ground states **3** and **3'** (**Scheme-II**).

4$_{cis}$ and **4´**$_{cis}$ are enantiomeric conformers with the same energy. The same is true for **5**$_{cis}$ and ***5´***$_{cis}$ which are mirror images. Diastromeric conformers **4**$_{trans}$ and **4´**$_{trans}$ are at different energies. So are **5**$_{trans}$ and **5´**$_{trans}$ (Table -1).

4$_{cis}$ is separable from **4**$_{trans}$, affording a temperature dependent NMR spectrum which allows quantitative dynamic analyses[14]. Two non-equivalent methyl groups appear in X'$_a$Y$_e$ (**4**$_{cis}$) and X'$_e$Y$_a$ (**4´**$_{cis}$) positions. NMR spectra of **4**$_{cis}$ and **4´**$_{cis}$ show methyl peaks as doublets at 1.03 and 1.22 ppm and CH absorptions as two quarteds at 2.68 and 3.47 ppm, respectively. Spectrum of *cis* conformers shows a change with temperature. At 95ºC, the pairs of methyl doublets and methine quartets each become one signal *per se* (still a doublet and a quartet, respectively). The spectrum at -40ºC of **4**$_{cis}$ is the same as that obtained at room temperature.



Scheme-II: Newman projections of conversion of dibenzo [*a,c*]cycloocta-5,8-dione derivatives, **1-5**, to their corresponding conformers **1´-5´**. Minima **1-5** are set at 0.00 kcal (left column). On such basis, relative energies of all the corresponding mirror images (right column) and transition states (TS, middle column) are calculated. Values shown in parentheses indicate E_a associated with **4´**$_{trans}$ and **5´**$_{trans}$ to their corresponding transition states, respectively

$\mathbf{4}_{trans}$ converts to its diasteromer, $\mathbf{4'}_{trans}$, through rotations around the biphenyl bond. Each of these *trans* conformers has two equivalent methyl groups groups $X_aX'_a$ and $X_eX'_e$ positions. They show only one signal for their methyl groups (doublet at 1.25 ppm) and one signal for their methine protons (broad quartet at 2.94 ppm), at room temerature. While at -40ºC, their methyl signals split into two doublets of unequal intensity (1.38 and 1.22 ppm in the ratio 9:5). Their methine signal also splits into two broad signals at 3.07 and 2.89 ppm, with a ratio of 9:5.

D-NMR inversion barrier found for $\mathbf{4}_{trans}$ is 14 kcal/mol. That of $\mathbf{4}_{cis}$ isomer is 18 kcal/mol. These are consistent with the trend calculated in this manuscript (Table-2). A relatively low barrier to rotational process in $\mathbf{4}_{trans}$ is justified by a weaker non-bonded interaction in the transition state (TS) between *trans* methyl groups. This is in contrast to a strong eclipsed interaction between the *cis* methyl groups in $\mathbf{4}_{cis}$ (**Scheme-II**). Both $\mathbf{4}_{\mathrm{cis}}$ and $\mathbf{4}_{trans}$ are capable of being equilibrated to a 4:1 mixture *via* enolization[14]. Related reaction path calculations are being carried out at this time.

Each of enantiomeric conformers $\mathbf{4}_{cis}$ and $\mathbf{4'}_{cis}$, $\mathbf{5}_{cis}$ and $\mathbf{5'}_{cis}$ has two different carbonyl groups: ones perpendicular to closer benzene ring and other *ca*. coplanar with closer benzene ring. Therefore simulated IR spectra show different absorbance for each carbonyl group in every enantiomeric conformer.

Interestingly, each of the diastromeric conformers $\mathbf{4}_{trans}$ and $\mathbf{4'}_{trans}$, $\mathbf{5}_{trans}$ and $\mathbf{5'}_{trans}$ has similar carbonyl groups with perpendicular position relative to closer benzene ring, consequently simulated IR shows only one absorbance for carbonyl group in every diastromeric conformer.

Consequently temperature dependent FT-IR spectra can be proposed as a powerful method for distinguish between *cis* and *trans* isomers of dibenzo [*a*,*c*]cycloocta-5,8-diones.

As a result, important factor that cause to observing two absorbance for each of $\mathbf{4}_{cis}$ and $\mathbf{4'}_{cis}$, $\mathbf{5}_{cis}$ and $\mathbf{5'}_{cis}$ and an absorbance for each of $\mathbf{4}_{trans}$ and $\mathbf{4'}_{trans}$; $\mathbf{5}_{trans}$ and $\mathbf{5'}_{trans}$ is relative position of carbonyl group and closer benzene ring. Obviously, carbonyl group that has ability of mesomery with benzene ring, give an absorbance in lower frequency. Orientations (semi-axial and/or semi-equatorial) of neighbourhood alkyls substituted on C_6 and C_7 have not important factor for observation of two (in *cis* isomers) and one (in *trans* isomers) absorbtions for carbonyl groups.

Conclusion

The order of energy barriers (E_a/kcalmol^{-1}) for stereo-specific inversions of 6XX´-7YY´-dibenzo[*a*,*c*]cyclooctadiene-5,8-dione, **1-5**, to their corresponding conformers, **1'-5'** is: $\mathbf{3} \rightleftharpoons \mathbf{3'}$ (34.00)> $\mathbf{2} \rightleftharpoons \mathbf{2'}$ (28.05) > $\mathbf{5}_{cis} \rightleftharpoons \mathbf{5'}_{cis}$ (27.21) > $\mathbf{5}_{trans} \rightleftharpoons \mathbf{5'}_{trans}$ (24.75) > $\mathbf{4}_{cis} \rightleftharpoons \mathbf{4'}_{cis}$ (22.35) > $\mathbf{4}_{trans} \rightleftharpoons \mathbf{4'}_{trans}$ (21.62) > $\mathbf{1} \rightleftharpoons \mathbf{1'}$ (19.47); for **1:** X=X´=Y=Y´=H, **2:** X=X´=Y=Y´=CH_3, **3:**

X=Y=H, X´=Y´= CH_3, **4**$_{cis}$: Y´=H, X´=Y=CH_3, **4**$_{trans}$: X´=CH_3, Y´=Y=H, **5**$_{cis}$: X=Y´=H, X´=Y= *i*-pr and **5**$_{trans}$: X=X´= *i*-pr, Y´=Y=H.

Our calculated data are consistent with the reported experimental results for **4**. Temperature dependent FT-IR spectra can be proposed as a powerful method for distinguish between *cis* and *trans* isomers of dibenzo [*a*,*c*]cycloocta-5,8-diones.

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