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Thermochemical Studies on 2,4,6-Triisopropylbenzophenone and Its Photo-isomer, 3′,5′-Diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol. Evaluation of Magnitude of Light Energy Stored in the Latter Molecule**

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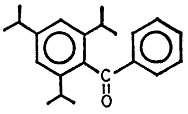
Standard energy of combustion and standard enthalpy of sublimation were determined for the title compounds with static bomb combustion calorimetry and with sublimation calorimetry, respectively. Derived standard enthalpies of combustion and of formation at 298.15 K were as follows: $\Delta H_c^\circ(c) = -(12354.3 \pm 1.8)$, $\Delta H_f^\circ(c) = -(304.6 \pm 3.4)$, and $\Delta H_f^\circ(g) = -(189 \pm 8)$ kJ mol^{-1}, respectively, for 2,4,6-triisopropylbenzophenone(**1**), and $\Delta H_c^\circ(c) = -(12440.6 \pm 1.6)$, $\Delta H_f^\circ(c) = -(218.3 \pm 3.3)$, and $\Delta H_f^\circ(g) = -(101 \pm 10)$ kJ mol^{-1}, respectively, for 3′,5′-diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol(**2**). The enthalpy change for the reaction: **1**(g)→**2**(g), of 88 kJ mol^{-1}, which may be supposed to be the magnitude of light energy stored in the latter molecule, has been discussed.

2,4,6-Triisopropylbenzophenone (**1**) undergoes photo-isomerization under irradiation in solution to afford 3′,5′-diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol (**2**) in quantitative yield[1)] and the latter compound is converted to the former quantitatively, when it is heated above 120 °C or reacted with base catalyst.[2)] The mechanism of the photo-isomerization has been elucidated,[2)] and the hindered rotation of **1**,[3)] the effect of 4′-substitution on the life-time of the triplet state of **1**,[4)] and the influence of ring substitution on the life-time of the biradical from **1**[5)] have been studied. Crystal structure of **1** has been determined by X-ray diffraction method.[21)]

In the present study, standard energies of combustion and standard enthalpies of sublimation were determined for **1** and **2** by calorimetric methods, in order to evaluate the magnitude of light energy, stored in the latter molecule as a result of the photo-isomerization reaction. The stored energy has been discussed in terms of the strain energy of the molecule.



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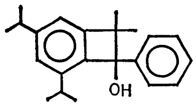

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Experimental

Materials. **1**[6)] and **2**[1)] were prepared according to the procedure described previously. **1** was purified by recrystallization from ethanol solution followed by vacuum fractional sublimation. **1** was treated throughout with minimum exposure to light. **2** was purified by recrystallization from petroleum ether solution followed by vacuum fractional sublimation. The procedure for **2** was undertaken at temperatures below 60 °C.

Combustion Calorimetry. An isoperibol rotating bomb calorimeter with a platinum-lined bomb, described elsewhere,[7,8)] was used without rotating the bomb. The calorimeter was calibrated by burning thermochemical standard benzoic acid(U.S. National Bureau of Standards SRM 39i) under certificate conditions. The certified specific energy of combustion of the benzoic acid $\Delta u_c(\mathrm{ba})$ is $-(26434 \pm 1)$ J g^{-1}, where uncertainty is our estimate of the standard deviation of the mean. Mean and standard deviation of the mean for the energy equivalent of the empty calorimetric system $\varepsilon(\mathrm{calor})$[12)] were determined to be (15157.32 ± 0.67) J K^{-1} from seven calibration experiments. A pellet of **1** was ignited in a deep crucible with a small lid[9)] together with a pellet of the thermochemical standard benzoic acid(approximately 0.25 g) in order to prevent incomplete combustion of **1**. The auxiliary benzoic acid contributed to approximately one fourth of total energy change. **2** was pressed into pellets and a pellet was burnt in an ordinary open crucible without a promoter at 3.040 MPa of oxygen pressure.

Nitric acid was determined by measuring the absorbance at 202 nm of the bomb solutions. Carbon dioxide recovery was determined for **2** by the method described elsewhere[8)] in order to examine the purity and/or completeness of combustion.

Sublimation Calorimetry. Sublimation enthalpy was measured as a function of temperature with the sublimation calorimetric system described elsewhere,[10)] in which a Calvet microcalorimeter (DAM, ambient to 473 K type), home-made sublimation apparatuses, and Knudsen-type sample containers were incorporated. Sublimation apparatus Mark II and sample containers Mark C were employed. Both the diameter and the depth of the effusion orifice were 1.0 mm. Thin-walled Pyrex glass tubes with a closed end were used for both compounds in order to prevent the samples from contact with the metallic container.

Auxiliary Quantities. Relative atomic masses were taken from the recommendation of IUPAC Commission on Atomic Weights (1977). Densities, specific heat capacities, $(\partial U/\partial p)_T$ values, and other auxiliary quantities, which were used to reduce weights to masses in vacuum and to deduce standard energies of combustion from calorimetric data, are collected in Table 1.

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Table 1. Auxiliary physical quantities of 2,4,6-triisopropylbenzophenone(**1**), 3′,5′-diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol(**2**), benzoic acid, and cotton

Compound	Formula	$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{c_p}{\text{J K}^{-1}\text{ g}^{-1}}$	$\frac{-(\partial U/\partial p)_T}{\text{J MPa}^{-1}\text{ g}^{-1}}$	$\frac{-\{\Delta U_c^\circ/M\}}{\text{J g}^{-1}}$
1	$C_{22}H_{28}O$	(1.11)$^{a)}$	(1.601)$^{a)}$	(0.052)$^{a)}$	—
2	$C_{22}H_{28}O$	(1.11)$^{a)}$	(1.601)$^{a)}$	(0.052)$^{a)}$	—
Benzoic acid	$C_7H_6O_2$	1.320	1.21	0.052	26413.6
Fuse	$CH_{1.86}O_{0.93}$	1.5	1.70	0.29	16507

V(bomb) = 0.3469 dm^3. a) Parenthesized values were estimated.

Table 2. Results of combustion calorimetric experiments on 2,4,6-triisopropylbenzophenone(**1**)

	Experiment						
	1	2	3	4	5	6	7
m'(compd)/g	0.51199	0.50934	0.50935	0.50622	0.51282	0.52518	0.52314
m''(auxil)/g	0.26424	0.25506	0.25192	0.25663	0.25306	0.24586	0.24904
m'''(fuse)/g	0.00214	0.00234	0.00258	0.00219	0.00243	0.00227	0.00254
$m^i(H_2O)$/g	1.150	1.131	1.096	1.117	1.092	1.108	1.116
p^i(gas)/MPa	3.040	3.030	3.040	3.040	3.040	3.040	3.040
θ_i/°C	23.14333	23.14841	23.15025	23.15616	23.14868	23.15248	23.14701
θ_f/°C	24.97957	24.96276	24.95958	24.96517	24.96893	24.99102	24.98630
$\Delta\theta_{corr}$/°C	0.02374	0.02451	0.02446	0.02438	0.02431	0.02299	0.02325
ΔU_{ign}/J	3.8	4.4	4.8	4.9	4.3	4.6	4.8
ε^i(cont)/J K^{-1}	20.46	20.33	20.21	20.30	20.20	20.28	20.31
ε^f(cont)J K^{-1}	21.84	21.69	21.57	21.66	21.57	21.67	21.70
ΔU_Σ/J	15.0	14.7	14.8	14.8	14.9	15.1	15.1
$-U_{IBP}$/J	27506.2	27160.7	27085.5	27081.3	27253.5	27551.5	27558.6
$-\{\Delta U_c^\circ/M\}$/kJ g^{-1}	39.9937	39.9937	39.9999	40.0058	40.0029	39.9956	39.9961
$-\Delta U_c^\circ$/kJ mol^{-1}	12336.8	12336.8	12338.7	12340.5	12339.6	12337.4	12337.5

Table 3. Results of combustion calorimetric experiments on 3′,5′-diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol(**2**)

	Experiment					
	1	2	3	4	5	6
m'(compd)/g	0.67759	0.67176	0.66857	0.66276	0.66979	0.67304
m'''(fuse)/g	0.00232	0.00206	0.00208	0.00184	0.00222	0.00182
$m^i(H_2O)$/g	1.094	1.122	1.123	1.121	1.100	1.102
θ_i/°C	23.12603	23.14599	23.14867	23.14726	23.14819	23.15170
θ_f/°C	24.95129	24.95521	24.94995	24.93364	24.95284	24.96429
$\Delta\theta_{corr}$/°C	0.02307	0.02302	0.02341	0.02408	0.02321	0.02305
ΔU_{ign}/J	3.9	4.3	4.0	4.0	4.3	4.3
ε^i(cont)/J K^{-1}	17.51	17.62	17.61	17.59	17.52	17.53
ε^f(cont)/J K^{-1}	18.93	19.02	19.01	18.98	18.92	18.94
ΔU_Σ/J	12.9	12.8	12.7	12.6	12.7	12.8
$-\Delta U_{IBP}$/J	27344.0	27101.0	26974.9	26738.6	27029.9	27151.9
$-\{\Delta U_c^\circ/M\}$/kJ g^{-1}	40.2791	40.2735	40.2768	40.2795	40.2808	40.2785
$-\Delta U_c^\circ$/kJ mol^{-1}	12424.8	12423.1	12424.1	12424.9	12425.3	12424.6
$\left\{\frac{m(CO_2,\text{ obsd})}{m(CO_2,\text{ calcd})}\right\}$	0.9993	0.9998	—	0.9995	0.9999	1.0001

Results

Results of combustion calorimetric experiments are presented in Tables 2 and 3 for **1** and **2**, respectively. Molar standard energies of combustion given in these tables refer to the following idealized combustion reaction at 298.15 K:

$$C_{22}H_{28}O(c) + (57/2)O_2(g) = 22CO_2(g) + 14H_2O(l).$$

Most of the symbols in these tables are essentially similar to those used by Hubbard *et al.*[12] ΔU_Σ denotes the sum of contributions from items 81—85 and 87—94 as defined by Hubbard *et al.*[12] $\{m(CO_2,$ obsd)/

Table 4. SUMMARY OF SUBLIMATION CALORIMETRIC RESULTS ON 2,4,6-TRIISOPROPYLBENZOPHENONE(**1**) AND 3′,5′-DIISOPROPYL-4,4-DIMETHYL-1,2-BENZOCYCLOBUTEN-3-OL(**2**)

$\frac{T}{\text{K}}$	$\frac{m}{\text{mg}}$	$\frac{E_{\text{calib}}}{\text{J}}$	$\left\{\frac{S_T}{S_B}\right\}$	$\frac{\Delta H_s^\circ(T)}{\text{kJ mol}^{-1}}$
		1		
353.5	36.15	1.594	7.8843	107.3
353.4	29.13	2.941	5.4596	107.8
363.7	64.83	4.258	5.2257	105.9
363.9	90.57	4.866	6.4016	106.1
		2		
353.2	25.21	1.477	5.9252	107.1
353.5	26.07	1.546	5.8885	107.7
363.1	56.17	4.864	4.0756	108.9
363.1	54.90	3.756	5.1570	108.8
364.0	83.54	4.564	6.4538	108.8
364.0	65.34	4.709	4.9787	110.6

$m(\text{CO}_2$, calcd)} is the ratio of the observed total mass of recovered carbon dioxide to the calculated one. Mean and standard deviation of the mean for the ratio were (0.9997±0.0001) for five experiments on **2**. While trace of soot was found in the crucibles in experiments Nos. 1, 3, 5, 6, and 7 for **1** and No. 3 and 5 for **2**, no correlation was found between the soot formation and the resultant standard energy of combustion. In addition, carbon monoxide was barely detected in the bomb gas. Mean and standard deviation of the mean for molar standard energy of combustion $\Delta U_c^\circ(\text{c})$ were $-(12338.18\pm0.55)$ and $-(12424.48\pm0.32)$ kJ mol^{-1} for **1** and **2**, respectively.

Results of sublimation calorimetric experiments are summarized in Table 4. Molar standard enthalpy of sublimation ΔH_s° $(T)$was calculated with the equation:

$$\Delta H_s^\circ(T) = E_{\text{calib}}(S_T/S_B)(M/m),$$

where E_{calib} is the electrical energy used for calibration, (S_T/S_B) is the ratio of the sublimation enthalpy to the calibration energy, which was determined by the calorimetric experiment, m is the mass of material that effused from the sample container, and M is the molar mass of the material.

For **1**, measurements were performed at two temperatures. Observed enthalpies of sublimation were subjected to a regression analysis for linear relations between two variables.[11] The derived function was as follows: ΔH_s° (T)/kJ mol^{-1}$=-0.1452(T/\text{K})+158.8$, with standard deviation from the fit of 0.3 kJ mol^{-1}. Standard enthalpy of sublimation at 298.15 K was evaluated by extrapolating the function to the reference temperature, since no heat capacity anomaly was found over the relevant temperature range in DSC heating curves of **1**. Derived standard enthalpy of sublimation at 298.15 K was (116±7) kJ mol^{-1}, where uncertainty is the one at the 95 per cent level.

The temperature dependence of $\Delta H_s^\circ(T)$ for **2** does not seem to be normal, although the observed values themselves are of reasonable magnitude: $\Delta H_s^\circ(T)$ should decrease with temperature rise. The observed values are supposed to include experimental errors of considerable magnitude, since the output voltage from the microcalorimeter was small. Although the output voltage could be increased by rising the temperature, this is not desirable for **2** owing to its thermal instability. Consequently, the observed values for **2**, given in Table 4, were averaged with equal weights, and the mean value was taken to be the value at the mean temperature. The value at 298.15 K was then estimated by assuming that the temperature dependence of $\Delta H_s^\circ(T)$ for **2** is identical with that of **1**. No heat capacity anomaly was detected in the DSC heating curves of **2** over the relevant temperature range. The estimated value at 298.15 K was (117±9) kJ mol^{-1}, where uncertainty was assigned rather arbitrarily.

Table 5. DERIVED THERMODYNAMIC QUANTITIES OF 2,4,6-TRIISOPROPYLBENZOPHENONE(**1**) AND 3′,5′-DIISOPROPYL-4,4-DIMETHYL-3-PHENYL-1,2-BENZOCYCLOBUTEN-3-OL(**2**) AT 298.15 K

Compound	**1**	**2**
$-\Delta U_c^\circ(\text{c})$/kJ mol^{-1}	12338.2±1.8	12424.5±1.6
$-\Delta H_c^\circ(\text{c})$/kJ mol^{-1}	12354.3±1.8	12440.6±1.6
$-\Delta H_f^\circ(\text{c})$/kJ mol^{-1}	304.6±3.4	218.3±3.3
ΔH_s°/kJ mol^{-1}	116±7	117± 9
$-\Delta H_f^\circ(\text{g})$/kJ mol^{-1}	189±8	101±10

Derived thermodynamic quantities are presented in Table 5. Uncertainties in this table are the overall values. The overall uncertainties for $\Delta U_c^\circ(\text{c})$ and $\Delta H_c^\circ(\text{c})$ are twice the overall standard deviation of the mean for $\Delta U_c^\circ(\text{c})$, $\{2s(\bar{U})_\Sigma\}$. $s(\bar{U})_\Sigma$ was calculated according to:

$$s(\bar{U})_\Sigma = [s(\bar{U})^2 + \{\Delta U_c^\circ(\text{c})s(\varepsilon)/\varepsilon(\text{calor})\}^2 + \{\Delta \bar{U}_c^\circ(\text{c})s(\text{ba})/\Delta u_c(\text{ba})\}^2 + \{M(\text{compd})\bar{m}(\text{ba})s(\text{ba})/\bar{m}(\text{compd})\}^2]^{1/2},$$

where $s(\bar{U})$, $s(\varepsilon)$, and s(ba) are the standard deviations of the mean for $\Delta U_c^\circ(\text{c})$, ε(calor), and $\Delta u_c^\circ(\text{ba})$, respectively, and $\bar{m}$(ba) and $\bar{m}$(compd) are the mean masses of the benzoic acid as used as the promoter and of the compound, respectively. For **2**, $m(\text{ba})=0$, and so the fourth term in the bracket of the equation is deleted. $s(\bar{U})_\Sigma$ amounted to 0.9 and 0.8 kJ mol^{-1} for **1** and **2**, respectively. Standard enthalpies of formation in the crystalline state were calculated by use of the following CODATA key values for thermodynamics:[13] $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -(393.51\pm0.13)$ and $\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) = -(235.830\pm0.042)$ kJ mol^{-1}, respectively, where uncertainties are those at the 95 per cent confidence level. Overall uncertainties for $\Delta H_f^\circ(\text{c})$ and $\Delta H_f^\circ(\text{g})$, $\delta(\Delta H_f^\circ$, c) and $\delta(\Delta H_f^\circ$, g), respectively, were calculated as follows:

$$\delta(\Delta H_f^\circ, \text{c}) = [\delta(\Delta U_c^\circ, \text{c})^2+\{22\times0.13\}^2 + \{14\times0.042\}^2]^{1/2}$$

and

$$\delta(\Delta H_f^\circ, \text{g}) = [\delta(\Delta H_f^\circ, \text{c})^2+\delta(\Delta H_s^\circ)^2]^{1/2},$$

where $\delta(\Delta H_s^\circ)$ is the uncertainty assigned to ΔH_s°(298.15 K).

Table 6. Comparison between calculated and observed values of ΔH_f°(g) for 2,4,6-triisopropylbenzophenone(**1**), 3′,5′-diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol(**2**), and related compounds

Compound	ΔH_f°(g)/kJ mol^{-1} Obsd	ΔH_f°(g)/kJ mol^{-1} Calcd Laidler[a]	ΔH_f°(g)/kJ mol^{-1} Calcd Group[b]	Δ[d] kJ mol^{-1} Laidler[a]	Δ[d] kJ mol^{-1} Group[b]
Benzene	82.9 ± 0.3[c]	83.1	82.8	−0.2	0.1
Isopropylbenzene	4.0 ± 1.0[c]	0.5	3.1	3.5	0.9
Benzophenone	59.0 ± 1.7[c]	43.9	61.1	16.1	−2.1
1	-189 ± 8[e]	−203.9	−178.2	15	−11
Cyclobutene	156.7 ± 1.5[c]	31.0	31.2	125.7	125.0
2	-101 ± 10[e]	−241.9	−233.8	141	123

a) Calculated values based on the Laidler sheme of bond energy:[15,16] $E(\text{C–C})=-0.1$, $E(\text{C}_b\text{–C}_b)=37.7$, $E(\text{C}_b\text{–C})=-14.5$, $E(C_b\text{–}C_{co})=-57.2$, $E(\text{C=C})=158.6$, $E(\text{C–H})_p=-14.1$, $E(\text{C–H})_s=-10.2$, $E(\text{C–H})_t=-7.1$, $E(\text{C}_b\text{–H})=-23.9$, $E(\text{C–O})=-77.5$, $E(\text{C=O})=-55.6$, and $E(\text{O–H})=-108.6$ kJ mol^{-1}. b) Calculated values based on the group contribution method:[22,23] $[\mathbf{C}_B\text{–(H)}]=13.8$, $[\mathbf{C}_B\text{–(C)}]=23.5$, $[\mathbf{C}\text{–(C}_B\text{)(C)}_2\text{(H)}]=-4.3$, $[\mathbf{C}\text{–(C)(H)}_3]=-42.3$, $[\mathbf{CO}\text{–(C}_B)_2]=-107.9$, $[\mathbf{C}_B\text{–(CO)}]=15.5$, $[\mathbf{C}_d\text{–(C)(H)}]=36.2$, $[\mathbf{C}\text{–(C}_d\text{)(C)(H)}]=-20.6$, $[\mathbf{C}\text{–(C)}_3(\text{C}_B)]=11.8$, $[\mathbf{C}\text{–(C}_B)_2\text{(C)(O)}]=-27.9$ (assumed), and $[\mathbf{O}\text{–(C)(H)}]=-158.4$ kJ mol^{-1}. c) Selected value given in Ref. 20. d) Destabilization energy: $\Delta=\Delta H_f^\circ(\text{g, obsd})-\Delta H_f^\circ(\text{g, calcd})$. e) Present result.

Discussion

Comparison between the standard enthalpies of formation in gaseous state of **1** and **2**, given in Table 5, leads to the standard enthalpy change of 88 kJ mol^{-1} for the isomerization reaction: **1**(g)→**2**(g). Since combustion and sublimation calorimetric experiments were carried out for **1** and **2** quite similarly, part of the uncertainties assigned to ΔH_f°(g) of **1** and **2** would be cancelled in calculating the difference in ΔH_f°(g) between **1** and **2**. Uncertainty for the difference is estimated to be around 10 kJ mol^{-1}. This enthalpy change may be identified with the magnitude of light energy stored in a molecule of **2** as a result of the reaction. Note that this enthalpy change is twice as large as that for the reaction: norbornadiene(g)→quadricyclane(g), with standard enthalpy change of 41.6 kJ mol^{-1} at 298.15 K.[14]

In order to interpret the large enthalpy change for the present isomerization, destabilization (strain) energy was evaluated for **1** and **2**, by use of the Laidler scheme of bond energy[15,16] and the group contribution method.[22,23] Calculated and observed standard enthalpies of formation in gaseous state are presented and compared with each other in Table 6, together with those of related compounds. As is shown in the table, both the schemes are capable of reproducing ΔH_f°(g) for benzene and isopropylbenzene reasonably well. The same is true by the group contribution method for benzophenone, but the Laidler scheme gives ΔH_f°(g) which is by 15 kJ mol^{-1} less negative than the experimental value. Destabilization energy for **1** was estimated to be 15 and −11 kJ mol^{-1} by the Laidler scheme and the group method, respectively. In view of the large uncertainty assigned to the experimental value of ΔH_f°(g) and possible uncertainty of at least 4 kJ mol^{-1} for the calculated values, these destabilization energies appear to be barely significant.

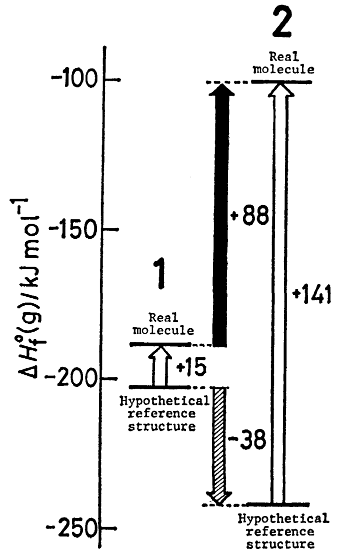

Fig. 1. Enthalpy diagram, based on the Laidler scheme of bond energy, of the gas phase photo-isomerization: 2,4,6-triisopropylbenzophenone(**1**)→3′,5′-diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol(**2**). Black and shaded arrows denote real and hypothetical enthalpy changes, respectively, for the reaction, and blank arrows denote estimated destabilization energies.

The destabilization energy of **2** amounts to 141 and 123 kJ mol^{-1} by the Laidler scheme and the group method, respectively. It is to be noted that these values are of similar magnitude with the destabilization energy of cyclobutene. The molecular structure of **2** has not been reported. However, according to X-ray diffraction studies on *cis*-3,4-dihalo-1,2-benzocyclobutenes (halogen=Cl, Br, and I)[17] and *cis*-1,2-benzocyclobuten-3,4-diol dinitrate,[18] carbon atoms in these molecules are almost coplanar, bond angles of the four-membered ring are similar with the corresponding ones of a cyclobutene molecule,[19] and the benzene ring is slightly elongated along the line connecting 3′ and 6′ carbon atoms. The presence of a highly strain-ed four-membered ring and the concomitant distortion of the benzene ring seem to be among the principal origins of the enhanced destabilization observed for **2**. Another posible contribution would come from the steric hindrance between the substituents of the four-membered ring. If this contribution is neglegibly small, the destabilization energy of 123 kJ mol^{-1} would be identified with the ring correction for a 1,2-benzocyclobutene ring in the group method.[23)]

In the meantime, if both **1** and **2** were neither stabilized nor destabilized as compared with each hypothetical reference structure, enthalpy change for the reaction: $\mathbf{1}(g) \rightarrow \mathbf{2}(g)$, would have been -38 kJ mol^{-1} (the Laidler scheme) or -46 kJ mol^{-1} (the group method), in contrast to the real value of 88 kJ mol^{-1}. The large positive enthalpy change for the real reaction is brought about by the large destabilization energy of **2**, which is far superior to the destabilization energy of **1** and also to the enthalpy change for the reaction between the hypothetical reference structures, as illustrated in Fig. 1, by use of the Laidler scheme. A similar diagram based on the group contribution method may be drawn.

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