

The Spectra of Thermochromic Substances. I¹

KI HONG KIM, LEE SMITH, THOMAS BEINECKE,² AND J. H. DAY

Department of Chemistry, Ohio University, Athens, Ohio

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The spectra of three thermochromic substances, rubrene, tetracyclone, and dimethylfulvene, have been examined over a range of temperature from -195 to 95° . As the temperature is lowered, rubrene spectra grow more intense and shift toward the red; tetracyclone absorption increases slightly and shifts toward the red; dimethylfulvene absorption increases but shows no red shift. When concentrations are corrected for thermal expansion, only the rubrene shows a notable increase in extinction coefficient.

Thermochromism is the visible, reversible change of color with temperature shown by several classes of molecules, most of them complex. The change may be spectacular, as with bianthrone, whose solutions turn from colorless to deep green on heating; for other reported thermochromic compounds the change in color ranges from slight to noticeable. Only for bianthrone, the spiropyrans, and the disulfides have the mechanisms of the thermochromic transitions been extensively studied.³

Possible mechanisms include: (1) a temperature-dependent equilibrium between differently colored forms, such as keto-enol, lactim-lactam, monomer-dimer, or equilibria involving configuration isomers, ring opening or the formation of ionic species or free radicals; (2) extension of conjugation in twisted or overcrowded molecules; (3) extrinsic effects such as thermal solvent expansion, temperature-sensitive solvent-solute interaction, or absorption band broadening caused by thermal redistribution of molecular rotation energy levels; (4) thermal excitation to low lying triplet states; (5) temperature-dependent fluorescence. A further possibility for solid materials is change in crystal state.

The purpose of this investigation was to examine the temperature dependence of the spectra of solutions of thermochromic compounds which can be classed as "overcrowded" molecules.

Experimental

Spectra were run on a Cary Model 14 spectrophotometer, using a specially made 1-cm. quartz cell mounted in a quartz dewar with optical windows (American Instrument Co.). Temperatures were regulated by filling the dewar with liquid nitrogen, with Dry Ice-acetone, or ice-salt. Higher temperatures were achieved with steam-heated thermal spacers in the cell compartment. Some of the spectra were also run on a Beckman D.U. spectrophotometer.

The EPA solvent and the methylcyclohexane were Spectrograde quality (Matheson Coleman and Bell). Solutions were accurately made up at room temperature, and concentrations at other temperatures were corrected for thermal expansion from the following data; each solvent was used in a half-filled tube 3.5 mm. in diameter and 35 cm. long, the meniscus marked at room temperature, and again at liquid nitrogen temperature. The difference in volume for EPA solvent was 22.5%. Data in the tables is for concentrations corrected for thermal expansion or contraction.

Several different samples of rubrene were used, some obtained from K and K Laboratories, some made in this laboratory by the method of Wittig and Waldi.⁴ Tetracyclone used was the product of K and K Laboratories. Dimethylfulvene was made in this laboratory.

Results

Rubrene.—Rubrene has been noted as thermochromic.⁵ Crystals of rubrene (5,6,11,12-tetraphenyl-naphthacene) appear brick red; powdered rubrene is bright orange. It darkens on heating and finally provides a ruby red melt which reverts to its normal color on cooling. Solutions, which are notably fluorescent, become more pink on heating, lighter and more yellow at low temperature.

Figures 1 and 2 show the spectrum of rubrene in EPA at various temperatures; the data appear in Table I.

Notable features are the increase in absorption intensity with decreasing temperature, as well as the regular shift of the whole absorption curve toward the red. The increase in absorption at low temperature remains considerable even when corrected for volume change of the solvent. Beer's law is followed in all the solvents used.

Tetracyclone.—Tetracyclone (tetraphenylcyclopentadienone) is a shiny black solid which melts to a deep purple. When a thin film of melt is allowed to cool between cover glasses to which pressure is applied at a point, it crystallizes in long needles radiating from the

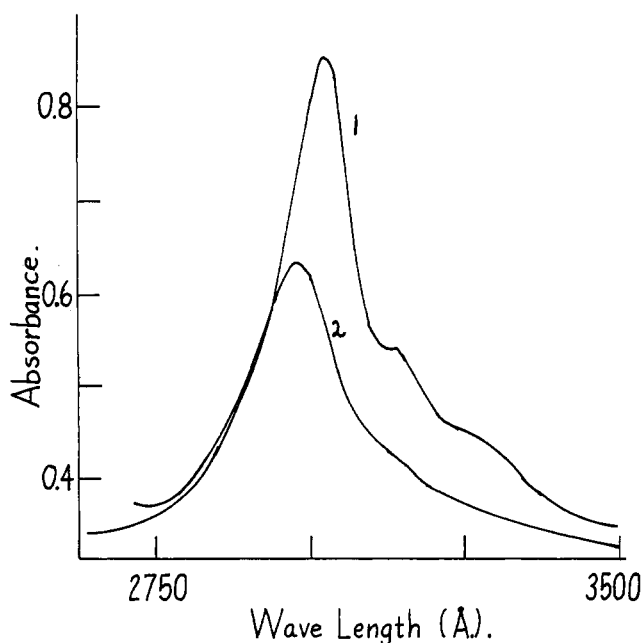


Fig. 1.—Absorption spectra of rubrene in EPA ($5.2 \times 10^{-6} M$): (1) at -195° ; (2) at 25° .

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(2) The data presented are abstracted from the M.S. theses of K. H. Kim and L. Smith, and an undergraduate honors project of T. Beinecke.

(3) J. H. Day, *Chem. Rev.*, **68**, 65 (1963).

(4) G. Wittig and D. Waldi, *J. prakt. Chem.*, **160**, 242 (1942).

(5) A. Schonberg, A. Mustafa, and W. Asker, *J. Am. Chem. Soc.*, **76**, 4134 (1954).

TABLE I
THE SPECTRA OF RUBRENE

Solvent	Temp., °C.	Absorption maxima (log extinction coefficient)			
EPA	-195	3025 (5.01)	4650 (3.74)	4970 (4.05)	5330 (4.10)
	-75	2995 (4.98)	4600 (3.65)	4960 (3.94)	5260 (3.97)
	-5	2985 (4.96)	4990 (3.62)	4885 (3.90)	5230 (3.91)
	26	2975 (4.95)	4585 (3.60)	4875 (3.87)	5220 (3.89)
Absolute ethanol	-75	2980 (4.98)	4600 (3.63)	4900 (3.92)	5250 (3.95)
	-5	2975 (4.96)	4580 (3.60)	4885 (3.88)	5225 (3.91)
	26	2970 (4.96)	4575 (3.59)	4875 (3.86)	5220 (3.88)
Methylecyclohexane	26	3000 (4.98)	4600 (3.63)	4910 (3.91)	5220 (3.93)
	95	2980 (4.93)	4600 (3.60)	4890 (3.87)	5225 (3.88)
Dimethyl phthalate	23	^a	4650 (3.61)	4940 (3.93)	5280 (3.95)
	83	^a	4680 (3.60)	4940 (3.90)	5260 (3.93)
Benzene ^b	Room	3030 (5.07)	4650 (3.79)	4950 (4.07)	5300 (4.08)

^a Not measured. ^b From G. M. Badger, R. S. Pearce, H. J. Rodda, and I. S. Walker, *J. Chem. Soc.*, 3151 (1954). See also ref. 10.

pressure point. These crystals are deep purple when observed by transmitted light looking along the long axis of the needles. Observed normal to the long axis, the crystals are transparent and colorless gray. Solutions of tetracyclone become brownish on heating, and more purple on cooling; color changes are definite without being striking. Figure 3 shows representative spectra; the data appear in Table II.

TABLE II
THE SPECTRA OF TETRACYCLONE

Solvent	Temp., °C.	Absorption maxima (log extinction coefficient)			
EPA	-195	2660 (4.36)	^a	5200 (3.03)	
	-75	2630 (4.40)	3460 (3.84)	5100 (3.10)	
	-5	2620 (4.37)	3370 (3.82)	5020 (3.12)	
	26	2620 (4.35)	3340 (3.81)	5020 (3.12)	
Absolute alcohol	26	2620 (4.36)	3400 (3.81)	^a	
	26	^a	3420 (3.83)	5120 (3.12)	
Benzene ^b	Room	^a	3420 (3.83)	5120 (3.12)	

^a Not measured. ^b S. B. Coan, D. E. Trucker, and E. I. Becker, *J. Am. Chem. Soc.*, 75, 900 (1953). For spectra in other solvents, see also p. 1057, Vol. I, Organic Electronic Spectral Data, Interscience Publishing Co., 1960.

The longest wave length band near 5100 Å. shows a regular shift toward the red as temperature is lowered, but there is no apparent change in intensity with temperature. The peak at 3400 Å. shifts to the red as expected, with little or no increase in intensity other than that caused by increased concentration due to solvent contraction.

Dimethylfulvene.—Dimethylfulvene when freshly prepared is a light yellow golden liquid which becomes much lighter in color at low temperature, and becomes a deep red near the boiling point. In dilute solution the color changes are similar but not as marked. Typical spectra are recorded in Fig. 4 and Table III.

TABLE III
THE SPECTRA OF DIMETHYLFULVENE

Solvent	Temp., °C.	Absorption maxima (log extinction coefficient)	
EPA	-195	2680 (4.24)	3500 (2.20)
	-75	2640 (4.21)	3500 (2.16)
	-5	2630 (4.19)	3500 (2.14)
	25	2630 (4.15)	3500 (2.12)
Benzene	25	^a	3600 (2.06)
Absolute alcohol	25	^a	3550 (2.06)

^a Not measured.

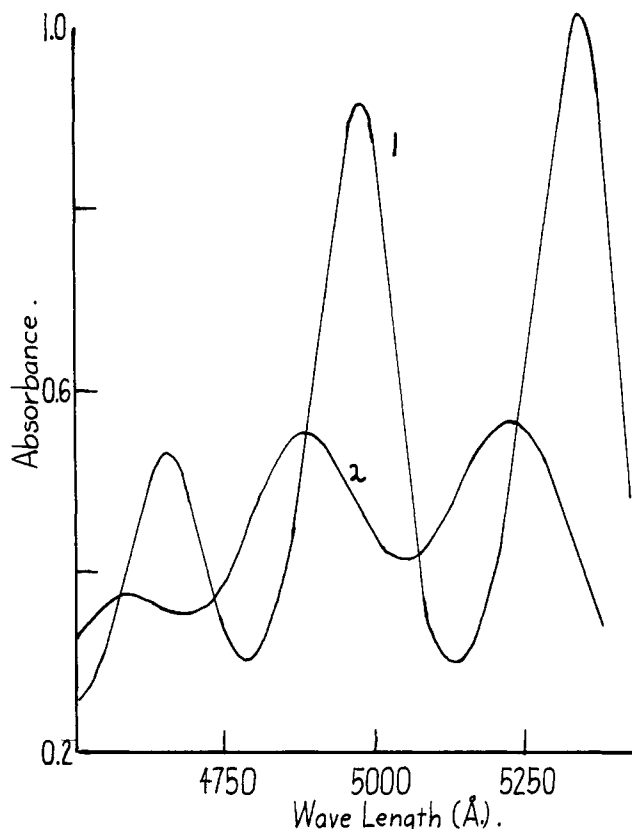


Fig. 2.—Absorption spectra of rubrene in EPA ($5.2 \times 10^{-5} M$): (1) at -195° ; (2) at 25° .

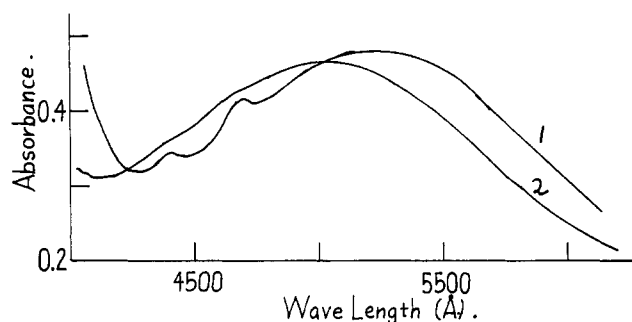


Fig. 3.—Absorption spectra of tetracyclone in EPA ($2.30 \times 10^{-4} M$): (1) at -195° ; (2) at 26° .

Discussion

In seeking an explanation for the thermochromism of rubrene, it is first necessary to decide whether there is a temperature-dependent equilibrium between two chemical species. The fact that Beer's law is obeyed over a range of concentrations rules out association equilibria, and e.p.r. spectra could detect no free radical formation.⁶ Rubrene is diamagnetic, which probably rules out an easily reached triplet state.⁷ The fact that no new peaks appear in the spectrum, and no old peaks disappear, makes the thermal generation of any new species of molecule unlikely as an explanation. Further evidence in this direction is the fact that a "heat of transformation" calculated from the usual plot of $\log \epsilon_{\max}$ vs. $1/T$ is so small as to be within experimental error, whereas a similar calculation for the thermochromic spiropyrans gives a value of 6 to 7 kcal./mole. The simultaneous shift in absorption maxima and in

(6) Courtesy of Schlumberger Corp.

(7) E. Muller and I. Muller-Rodloff, *Ann.*, 517, 134 (1935).

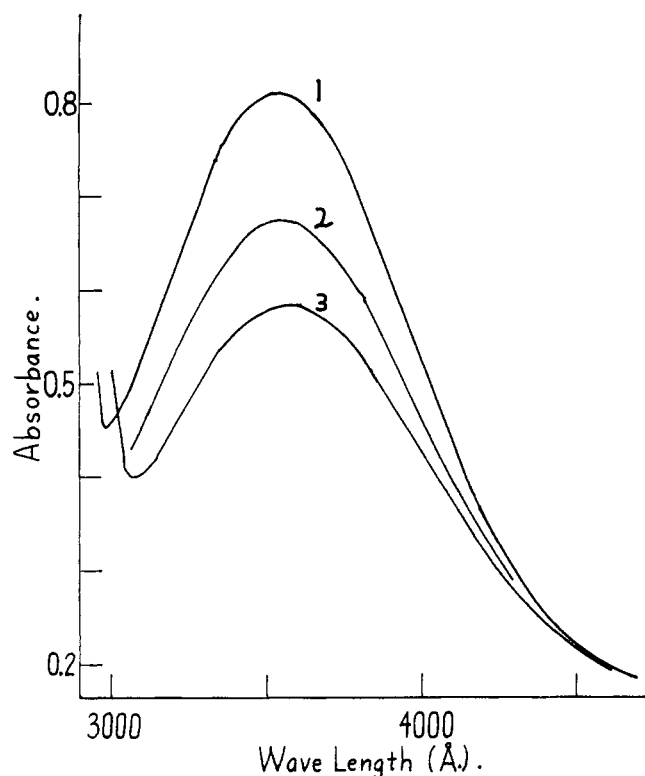


Fig. 4.—Absorption spectra of dimethylfulvene in EPA ($3.2 \times 10^{-3} M$): (1) at -195° ; (2) at -75° ; (3) at 25° .

intensity as temperature is changed results in several isosbestic points, whose existence is further argument for the existence of a single chemical species.⁸

Since the eye looks *at* a sample, while the spectrophotometer looks *through* a sample, a room temperature solution of rubrene in dimethyl phthalate was compared visually with a sample heated to 200° . Viewed by reflected light the cool solution was brilliant orange-red with a noticeable yellow fluorescence, while the hot solution was a warm red with no trace of yellow. When viewed by transmitted light, both the hot and the cold solutions appeared orange, with little noticeable difference.

The shift of absorption peaks toward the red can be accounted for by the increase in refractive index of solvent as temperature is lowered.⁹ Badger and Pearce¹⁰ measured the spectrum of rubrene in nineteen different solvents and found a linear relationship between red shift and a function of the refractive index of the solvent. From this data they estimate that cooling to liquid nitrogen temperatures should cause a shift to the red of about 30 to 80 Å., which estimate is supported by the present data. However, they found that a slight decrease in absorption intensity accompanied the red shift caused by change of refractive index at room

temperature, the reverse of what happens when the red shift is caused by temperature lowering.

Clar¹¹ measured spectra of several polynuclear hydrocarbons at room temperature and liquid nitrogen temperature. He also found a red shift of the order of 20 to 30 Å., and noted that the difference in intensities between maxima and minima more than doubled in going to the lower temperature. Similar results have been reported for naphthalene.¹² The increase in absorption intensity remains to be accounted for.

Tetracyclone and Dimethylfulvene.—The visible color change in tetracyclone may be ascribed to the considerable red shift together with the apparent increase in intensity of the 3500 Å. portion of the curve. The dimethylfulvene spectrum consists of a strong band in the ultraviolet and a weak broad band extending from 3000 Å. to beyond 4500 Å. The only change of visible spectrum is that of apparent increase in absorption intensity with decreasing temperature, which is almost entirely a solvent contraction effect; there is no red shift. It seems remarkable that the eye should perceive so definite a color change due to a simple thermal expansion.

Examination of the spectra will show that they behave differently as the temperature is lowered. The minima between peaks for rubrene have about the same red shift as do the peaks, and the minima lie lower as the peaks rise higher. For tetracyclone the minima have a smaller red shift than do the peaks; the order of intensity of the minima at 3100 Å. are in the same order as the peaks at 3500 Å., while the minima at about 4200 Å. have almost equal intensity. In dimethylfulvene the minima at 3000 Å. follow the order of the peaks.

The red shifts of rubrene and tetracyclone correspond to increase in solvent refractive index; the lack of any shift in the dimethylfulvene 3500 Å. peak seems remarkable from this standpoint, unless the phenyl groups on the first two compounds are somehow involved in the red shift.

Summary

The spectrum of rubrene undergoes a red shift with decreasing temperature which can be accounted for by increase in refractive index of solvent; the absorption intensity is approximately doubled at each absorption maximum as the temperature is lowered from room temperature to -195° . The observable thermochromism is believed due to the real spectral changes plus a temperature-dependent fluorescence. The apparent thermochromism of tetracyclone is probably due primarily to the red shift with lowering temperature. The apparent thermochromism of dimethylfulvene may be due to thermal expansion alone.

(8) J. R. Morrey, *J. Phys. Chem.*, **66**, 2169 (1962).

(9) W. J. Potts, Jr., *J. Chem. Phys.*, **23**, 65 (1955).

(10) G. M. Badger and R. S. Pearce, *Spectrochim. Acta*, **4**, 280 (1951).

(11) E. Clar, *ibid.*, **4**, 116 (1950).

(12) A. N. Terenin and V. L. Ermaliev, *Dokl. Akad. Nauk, SSSR*, 547 (1952).