Structural Aspects of the Mechanical and Thermal Dissociation of the Central Bond in 2,2'-Bis(2,3,4-triarylchromenyl)s

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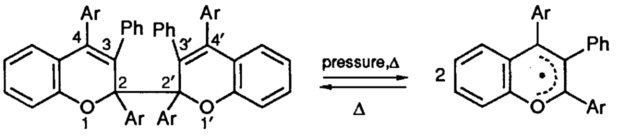
2,2'-Bis(2,3,4-triphenylchromenyl) (**1a**) has been shown to undergo reversible homolytic cleavage of the C(2)–C(2') bond to give green-coloured chromenyl radicals when subjected to mechanical force or heating in the solid state. 2,4-Bis-(*p*-chlorophenyl) (**1b**), 2,4-bis-(*p*-tolyl) (**1c**), 2,4-bis-(*p*-methoxyphenyl) (**1d**), and 2,4-bis-(*p*-bromophenyl) (**1e**) derivatives have been synthesized, and substituent effects on the radical dissociation investigated. Upon pressing **1b** exhibits the highest degree of dissociation, while thermal dissociation is facilitated by electron-releasing methyl (**1c**) and methoxy (**1d**) groups. Dissociation enthalpies (ΔH) for **1a–e** in dichloromethane solutions are evaluated to be 12–15 kcal mol^{-1}. The small values of ΔH are considered to be mainly due to overcrowding around the C(2)–C(2') bond. MMP2 calculation predicts that *meso*-**1a** is more stable than the (±)-isomer and the lowest-energy conformation of *meso*-**1a** is a centrosymmetric *anti* form. In the optimized geometry of *meso*-**1a** C(2)–C(2') the bond length is calculated to be 1.584 Å, which is rather longer than a normal C_{sp^3}–C_{sp^2} bond. AM1 calculations give similar results and suggest that through-bond interactions between the lone-pairs on the oxygen atoms and/or 2- and 2'-aryl groups are not significant compared with the steric repulsion.

A reversible colour change caused by applying and removing pressure has been termed as piezochromism. Only a few compounds such as bianthrone,[1] bis(triarylimidazolyl)s,[2] and bis(benzofuranonyl)s[3] have been reported to exhibit piezochromism, and mechanistic studies have been very limited. Bis(2,3,4-triphenylchromenyl) (**1a**) was synthesized by Löwenbein and Rösenbaum in 1926[4] and reported to exhibit both piezo- and thermo-chromism in the solid state.[5] As the coloured species they proposed the chromenyl radical formed by homolysis of the C(2)–C(2') bond (Scheme 1). In connection with our interest in the homolysis of a sterically hindered C–C covalent bond by a relatively small amount of mechanical energy, we intended to further investigate the piezo- and thermo-chromic properties of **1a** in order to clarify the mechanism of the bond dissociation at a molecular level. In this study *para*-substituted derivatives **1b–e** were synthesized and substituent effects on the homolysis of the C(2)–C(2') bond upon pressing or heating were quantitatively studied by means of EPR spectrometry.



1a–e

1 a; Ar = Ph
b; Ar = p-ClC$_6$H$_4$
c; Ar = p-MeC$_6$H$_4$
d; Ar = p-OMeC$_6$H$_4$
e; Ar = p-BrC$_6$H$_4$

Scheme 1

The central C–C bond in **1** is expected to be longer than a normal C_{sp^3}–C_{sp^3} bond and the elongation of this bond may be caused not only by overcrowding around the bond but also by through-bond orbital interactions[6] between lone-pairs on the oxygen atoms and/or the aryl groups at the 2- and 2'-positions. Unfortunately, **1a–e** were all powdery solids and no single crystals suitable for X-ray study could be obtained. So in order to clarify a relationship between structure and reactivity for the bond dissociation, conformational analysis of **1a** was carried out by MM and MO calculations.

Table 1 g-Value and spin concentration of radicals formed from **1a–e** by applying pressure of 400 kg cm^{-2}

Compound	g	Spin concentration × 10^{-22}/ mol of dimer
1a	2.0037	1.57
1b	2.0040	3.42
1c	2.0038	0.216
1d	2.0039	0.183
1e	2.0045	1.06

Results and Discussion

Bond Dissociation under Pressure in the Solid State.—The colourless solid of **1a** turned green when compressed with a press or ground in a mortar, and the green-coloured sample exhibited a strong EPR signal. On standing under atmospheric pressure at 10–20 °C the signal intensity was gradually reduced as the colour faded. At higher temperatures (< 70 °C) the signal intensity decreased faster.† Compounds **1b–e** exhibited similar piezochromic properties (Table 1). These results support the theory that the coloured species derived from **1a–e** under pressure are the chromenyl radicals formed by homolysis of the

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† The decay rates of the radical concentrations were measured at 50 and 70 °C and found to obey a third-order rate law. It is difficult to explain the results of the kinetics now, but it is noteworthy that in the piezochromism of bis(2,3,4-triphenylimidazolyl) the kinetics of the radical recombination in the solid state also obeyed a third-order rate law.[2]

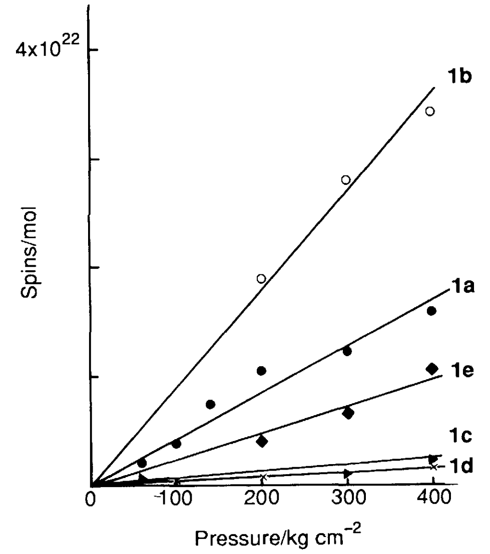


Fig. 1 Pressure dependence of the spin concentration for **1a**–**e**

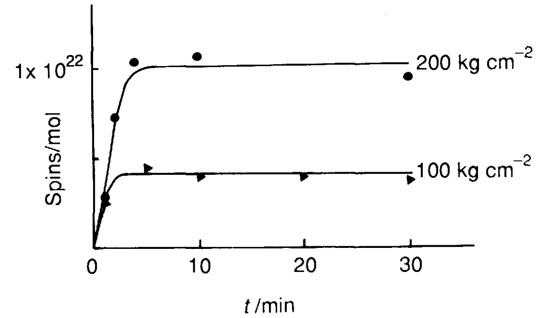


Fig. 2 Variation of spin concentration of **1a** under different compression times

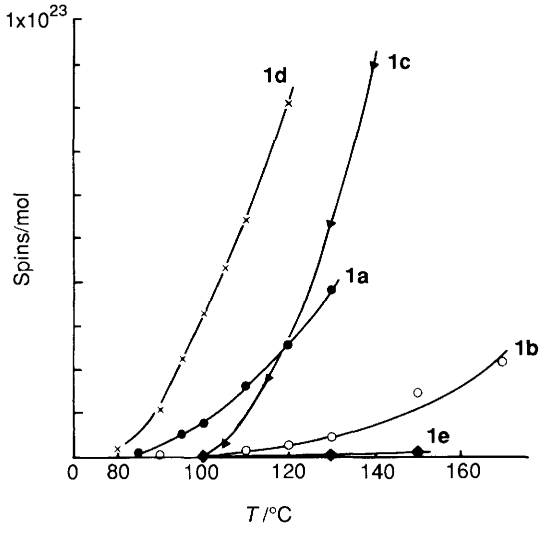


Fig. 3 Temperature dependence of the spin concentration for **1a**–**e** in the solid state

C(2)–C(2′) bond. Fig. 1 shows the spin concentration, *i.e.* the number of spins per mole of dimer, found after applying various pressures for 30 min. In the pressure range 0–400 kg cm^{-2} the radical concentration increased almost linearly with increased pressure. The spin concentration under pressure is in the order **1b** > **1a** > **1e** > **1d** ≈ **1c**. The *p*-chloro substituent in **1b** facilitates dissociation, while electron-releasing substituents such as methyl and methoxy groups tend to inhibit the dissociation. On the other hand, when the compression time was varied at a constant pressure of 100 or 200 kg cm^{-2}, the radical concentration for **1a** rapidly increased up to 2 min, at which time a plateau was reached (Fig. 2). From these observations bond dissociation of the central bond in **1a**–**e** was proved to occur under the effect of relatively low pressure. However, when a solid sample of **1a** was suspended in oil and a pressure of 6000 kg cm^{-2} was applied for 5 min, the solid remained colourless and no EPR signal was observed. The different dissociation behaviour may be attributable to a difference in the mode of application of pressure to the solid sample. In the case of grinding or pressing with a press each particle of the sample is subjected to anisotropic force; on the other hand, when suspended in an oil, pressure is applied to the sample from all directions. Bond dissociation of **1a** occurred only in the former case. Although the detailed mechanism is still an open question, these results seem to suggest that the bond dissociation of **1a**–**e** in the solid state is a kind of mechanochemical reaction caused by rubbing rather than high pressure, *i.e.*, it is not a piezochromic but a 'mechanochromic' phenomenon.

Table 2 Thermodynamic parameters of **1a**–**e** in deaerated dichloromethane solutions

Compound	$K^a/10^{-5}$ dm^3 mol^{-1}	ΔH^b/kcal mol^{-1}	ΔS/cal mol^{-1}K^{-1}
1a	8.62	12.2	23
1b	7.26	14.0	29
1c	17.0	13.4	28
1d	10.6	12.9	26
1e	3.65	14.8	30

[a] At 293 K. [b] Determined between 253 and 313 K.

Thermal Dissociation in the Solid State.—When **1a**–**e** were heated in the solid state, a green colour developed and this colour disappeared on cooling. The coloured solid showed an intense EPR signal, which showed the same *g* value and linewidth as that obtained after applying pressure. These results indicated that thermochromism of **1a**–**e** is due to reversible dissociation of the C(2)–C(2′) bond, and the coloured species is an identical radical to that formed under pressure.

Fig. 3 shows the temperature dependence of the spin concentration for **1a**–**e**. For each compound thermal dissociation began at *ca.* 80 °C and the spin concentration increased with a rise in temperature until the decomposition point was reached. The degree of dissociation obtained just before each decomposition temperature is in the order **1d** ≈ **1c** > **1a** > **1b** > **1e**. Electron-releasing methyl and methoxy groups tend to facilitate the dissociation, while halogens inhibit it. The opposite tendencies of substituent effects on dissociation under pressure and by heating suggest that different factors govern the degree of dissociation in these two processes, although they give rise to identical radical species. Furthermore, the results rule out the possibility that the mechanochemical bond dissociation could occur by heat of rubbing.

Thermodynamic Parameters of Dissociation in Solutions.—The dissociation enthalpy ΔH_{diss} and entropy ΔS_{diss} of **1a**–**e** were estimated in degassed dichloromethane solutions. As seen in Table 2, although *para*-substituents did not have a pronounced influence on the dissociation enthalpy, a comparison of dissociation constants *K* among **1a**–**e** showed that methyl and methoxy groups tended to increase *K*, while halogens seemed to diminish it. This tendency is in accordance with the substituent effects on thermal dissociation in the solid state.

For a few other compounds which undergo homolytic dissociation on pressing and heating, ΔH_{diss} values have been reported: 20–25 kcal mol^{-1} for bis(benzofuranoyl)s[3] and 26

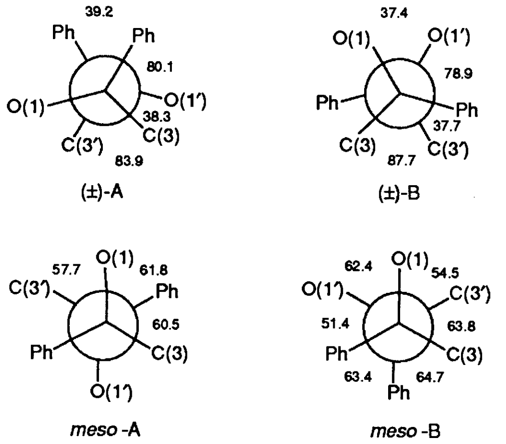


Fig. 4 Newmann projections of the stable conformations for (±)- and *meso*-**1a**

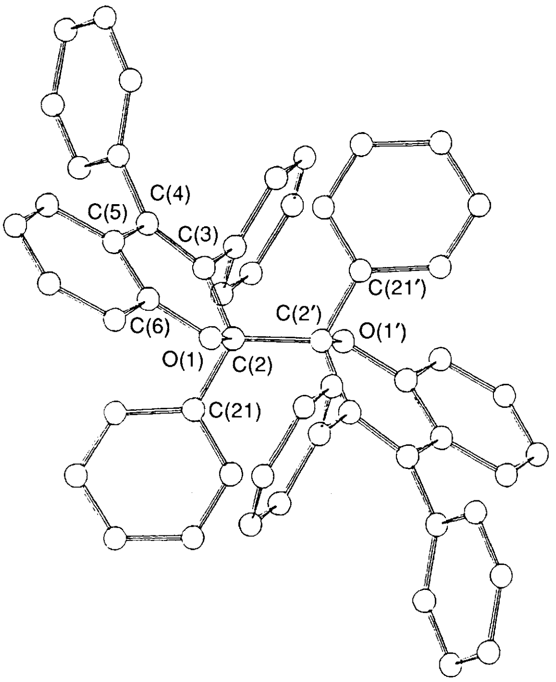


Fig. 5 MMP2 optimized structure of *meso*-**1a** with the atom-numbering

Table 3 Steric energy/kcal mol^{-1} of (±)- and *meso*-**1a**

	(±)-A	(±)-B	*meso*-A	*meso*-B
Total[a]	−0.98 (6.36)	0.10 (7.44)	−7.34 (0.00)	−1.19 (6.15)
Compression	6.30	5.98	5.47	5.72
Bending	12.84	11.78	13.65	13.12
Stretch-bend	0.30	0.34	0.39	0.34
VDW 1,4-	41.40	40.22	38.97	40.79
other	−18.99	−22.13	−18.97	−19.37
Torsional	−44.40	−38.03	−47.82	−43.71
Dipole	1.46	1.95	0.96	1.92

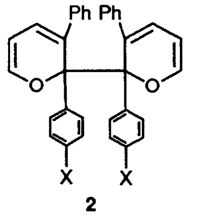
[a] Values in parentheses are relative to *meso*-A.

kcal mol^{-1} for bis(triphenylimidazolyl).[2,*] The ΔH_{diss} values of 12–15 kcal mol^{-1} obtained for **1a**–**e** are lower by as much as 10 kcal mol^{-1} than that for these compounds. It is likely that the difference is, at least partly, due to more serious steric hindrance around the central C–C bond of **1a**–**e** than the others.

MMP2 and AM1 *Calculations*.—Compound **1a** can exist as either (±)- or *meso*-isomers, but it is difficult to elucidate experimentally which isomer is actually obtained. Therefore, stable conformers were calculated for both isomers and their stabilities were compared with each other. MMP2[7a,b] calculations for (±)-**1a** gave two stable conformations with C_2 symmetry [(±)-A and (±)-B], and for *meso*-**1a** a centrosymmetric (*meso*-A) and a gauche form (*meso*-B) were obtained as stable conformers (Fig. 4). Among these conformers *meso*-A was shown to have the lowest total steric energy (Table 3).

Fig. 5 shows the optimized molecular structures of *meso*-A with the atom-numbering. An important feature of this conformation is that the two phenyl rings at the 2- and 2′-positions are coplanar with the C(2)–C(2′) bond. The dihedral angles between the chromenyl plane and the phenyl groups at the 3- and 4-positions are 76.6 and 72.6° respectively. The MMP2-calculated C(2)–C(2′) bond lengths of *meso*- and (±)-**1a** (Table 4) may look comparable to the average bond length of 1.588 Å, obtained from X-ray studies of hexasubstituted ethanes $R_3C–CR_3$ ($R = C_{sp^3}$).[8] However, it must be taken into consideration that the six substituents at the central bond of **1a** are all electronegative in comparison with C_{sp^3}, hence the 'equilibrium' distance of this bond must be shortened by *ca.* 0.02 Å.[9a,b] For this reason, we think that the C(2)–C(2′) bond in **1a** is more strained than in the case of $R_3C–CR_3$ ($R = C_{sp^3}$).

In order to study the effects of through-bond interactions between the lone-pair electrons on the oxygen atoms and/or the aryl groups at the 2- and 2′-positions, semi-empirical molecular orbital AM1[10] calculations were carried out for model compounds (±)- and *meso*-**2a**. A comparison of heat of formation between (±)- and *meso*-**2a** indicates that *meso*-**2a** will be more stable by 2.9 kcal mol^{-1} than (±)-**2a**, which is in a relatively good agreement with the result obtained by MM calculation for **1a**. The molecular structures optimized by the two methods were very similar to each other except for some slight differences in bond lengths (Table 4). The small difference in C(2)–C(2′) bond length suggests that the contribution of through-bond interaction to elongation of this bond is much smaller than that of steric hindrance.



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X = H (**2a**), CH_3,Cl,O^-,CN

To estimate substituent effects on the molecular structure of **1**, AM1 optimizations were further carried out for *para*-substituted model compounds **2** with CH_3, Cl, O^-, and CN groups. However, the structural parameters including C(2)–C(2′) bond length were little affected by the electronic nature of these substituents. This result may be rationalized as follows: in the optimized conformations of **1** and **2** the π-orbitals on the aryl rings at the 2- and 2′-positions are almost perpendicular to the σ and σ* orbitals on the C(2)–C(2′) bond, and therefore these orbitals cannot overlap sufficiently to bring about significant interactions. Compounds **1b**–**e** also contain *para*-substituted phenyl groups at the 4- and 4′-positions, but it is likely that the electronic nature of the substituent is poorly

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[*] 1 cal = 4.184 J.

Table 4 Selected bond lengths/Å of **1a** and **2a**

	(±)-**1a**	*meso*-**1a**	(±)-**2a**		*meso*-**2a**	
	MMP2	MMP2	MMP2	AM1	MMP2	AM1
C(2)–C(2′)	1.581	1.584	1.586	1.603	1.584	1.590
O(1)–C(2)	1.431	1.426	1.429	1.456	1.432	1.455
C(2)–C(3)	1.536	1.534	1.540	1.520	1.537	1.520
C(2)–C(21)	1.549	1.546	1.539	1.519	1.546	1.524
C(3)–C(4)	1.357	1.353	1.354	1.359	1.352	1.356
C(4)–C(5)	1.469	1.465	1.453	1.438	1.454	1.440
C(5)–C(6)	1.402	1.401	1.345	1.350	1.344	1.532
C(6)–O(1)	1.366	1.363	1.364	1.372	1.362	1.368

Table 5 Analytical and MS spectral data for bischromenyls **1a**–**e**

Compound (Formula)	M.p./°C (decomp.)	Found (%) (Required)				MS (70 eV) *m/z* (%)
		C	H	Cl	Br	
1a	120–126	88.7	5.3			359
($C_{54}H_{38}O_2$)	(lit.,[4] 150–165)	(90.2	5.3)			($M^+/2$, 100)
1b	150–160	74.8	4.0	16.85		427
($C_{54}H_{34}Cl_4O_2$)		(75.7	4.0	16.55)		($M^+/2$, 100)
1c	147–150	89.3	6.05			388
($C_{58}H_{46}O_2$)		(89.9	6.0)			($M^+/2$, 100)
1d	110–130	80.8	5.5			419
($C_{58}H_{46}O_6$)		(83.0	5.5)			($M^+/2$, 32)
1e	151–156	62.6	3.3		30.25	517
($C_{54}H_{34}Br_4O_2$)		(62.7	3.3		30.9)	($M^+/2$, 100)

transmitted to the C(2)–C(2′) bond due to the large dihedral angle between the aryl plane and the chromenyl ring.

Experimental

IR spectra were recorded on a JASCO A-302 spectrometer as KBr disks. EPR spectra were recorded on a JEOL JES-FE2XG spectrometer equipped with an ES-DVTI variable temperature controller. Spin concentrations were obtained by using an ESPRIT23 EPR data system with 4-hydroxy-2,2,6,6-tetramethylpyrrolidin-1-oxyl (TEMPOL) as a standard. Mass spectra were recorded on a JEOL DX-300 mass spectrometer. M.p.s. were obtained with a Yanagimoto micro apparatus and are uncorrected.

Synthesis of **1a**–**e**.—Bischromenyl **1a**–**e** were synthesized according to the method of Lowenbein and Rosenbaum.[4] These compounds thermally dissociate to the corresponding radicals on dissolution into degassed organic solvents. Therefore, the obtained precipitates were carefully washed with 10% aq. H_2SO_4, water, acetone, diethyl ether, and then hexane to remove the concomitant magnesium salts and other impurities. Analytical and MS spectral data are listed in Table 5.

Determination of the Spin Concentrations.—Dissociation under pressure in the solid state. To a solid sample (20 mg) was applied various pressures (50–400 kg cm^{-2}) with a press. The sample was powdered and put into a sample tube, and immediately EPR spectra were recorded at room temperature to obtain spin concentrations.

Dissociation on heating in the solid state. A solid sample (25 mg) in an EPR sample tube filled with Ar gas, was set in the EPR cavity which was thermostatted at the desired temperature prior to each measurement. After standing at this temperature for 30 min, EPR spectra were recorded.

Measurement of Thermodynamic Parameters of **1a**–**e** *in Dichloromethane Solutions.*—Since the radical formed from **1** was very sensitive to oxygen, sample solutions were prepared as follows: 0.5 cm^3 of dichloromethane in an EPR sample tube was cooled with liquid nitrogen and degassed. A solid sample weighed in a glass capillary was put into the tube containing the frozen solvent and degassed. When it was allowed to warm up to room temperature the solid sample completely dissolved. Spin concentrations were measured at 4–7 different temperatures between 233 and 293 K by EPR spectrometry. Each plot of ln K *vs.* $1/T$ gave a straight line (r = 0.998–0.999) and from the slope and intercept ΔH_{diss} and ΔS_{diss} were calculated. For each sample of **1a**–**e**, 2–4 similar experiments were carried out and the experimental error of ΔH was within ± 0.4 kcal mol^{-1}.

Calculations.—Molecular mechanics calculations were carried out on an HP Apollo DN10010 or an IBM 4381-R24 computer. AM1 calculations were performed using a locally updated MOPAC program, version 4.01[11] on a HITAC M-680 computer at the Computer Centre of the University of Tokyo.

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