Radical Dissociation of 2,2′-Bis(2-aryl-3-benzothiophenonyl)s by Mechanical Energy

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On applying pressure with a press in the solid state, the title compounds undergo homolysis of the central C–C bond to give green-colored radicals. X-Ray structure analysis for *p*-chloro derivative showed that the central C(2)–C(2′) bond was not elongated but had a normal distance (1.576 Å) as a hexa-substituted C_{sp^3}–C_{sp^3} bond. The amount of the radical formed by mechanical energy depended on the substituents on the 2-phenyl rings and on the solvent of crystallization. As for the crystals containing no solvent, *p*-bromo and *p*-chloro derivatives showed higher reactivity than the unsubstituted compound, probably due to smaller dissociation enthalpy. The radical dissociation was suppressed by the presence of some solvent of crystallization. In the solvated crystals, the excess energy supplied by external mechanical energy would be transferred mainly to vibrational modes of the solvent molecules rather than to the substrate.

A few organic compounds such as bis(2,4,5-triphenylimidazolyl),[1] 3,3′-bis(3-aryl-2-benzofuranonyl)s,[2,3] and 2,2′-bis(2,3,4-triarylchromenyl)s,[2] have been known to exhibit a color change on pressing in the solid state (Chart 1). The developed color gradually changed back to the original one and this phenomenon could be observed repeatedly. The colored species was identified as a stable radical which was formed by homolytic cleavage of the central bond. This observation seems strange because the dissociation reaction causes an increase in the number of molecules in spite of the decrease in the volume of the solid by compressing. Recently we pointed out that the system was not equilibrated during such a sudden increase of external pressure.[4] The formed radicals were long-lived enough to detect after removal of the external pressure because the dimerization was slow in the solid state. The term "mechanochromism" (instead of piezochromism) was proposed for a color change on applying mechanical energy.[4] Although the studies on the structural aspects of these compounds indicated the central bond was lengthened by intramolecular steric repulsions,[4—6] the detailed mechanism for the bond cleavage by mechanical energy is not fully understood.

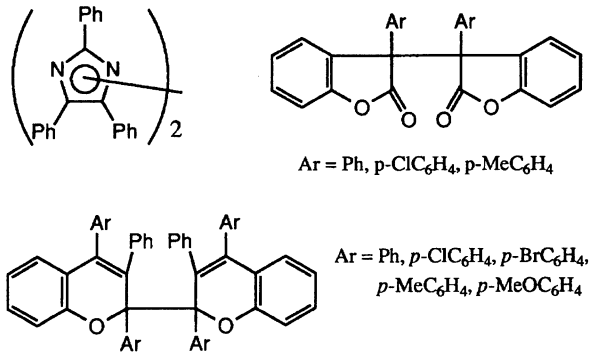
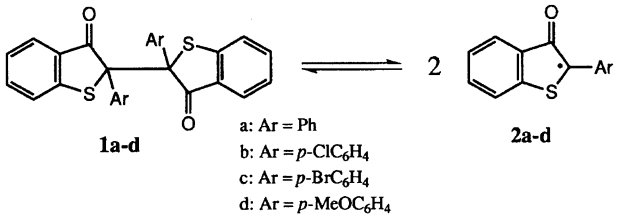


Chart 1.

2,2′-Bis(2-phenyl-3-benzothiophenonyl) (**1a**) was synthesized by Kalb and Bayer,[7] who reported it to exhibit thermochromism. Baldock et al. established on the basis of ESR investigation that this reversible color change was due to dissociation to green-colored radical **2a** and recombination to dimer **1a** (Eq. 1).[8] On applying pressure of 400 bar with a press in the solid state, **1a** exhibited a color change from pale yellow to green, indicating the formation of **2a**. When recrystallized from benzene **1a** formed an inclusion compound with 1 : 1 stoichiometry (**1a** : C_6H_6), while neat crystals of **1a** were obtained from a $CHCl_3$ solution.[3] Such a polymorphic compound can become a good tool for the study of solid-state reactions. To clarify how the mechanical energy causes homolytic cleavage of the covalent bond, dissociation of **1a—d** on pressing with a press has been investigated. In this paper, the effects of *p*-substituents on the 2-phenyl rings and of the solvent of crystallization are discussed.



(1)

Results and Discussion

Sample Preparation. On recrystallization from C_6H_6 or $CHCl_3$, **1a—c** formed crystalline inclusion compounds. TG-DTA curves of these solids indicated that the stoichiometry of **1** : solvent was either 1 : 1 or 1 : 2 (Table 1). The included

Table 1. Formation of Inclusion Compounds of **1a**—**d** with Solvents

Compd	Solvent	**1** : Solvent
1a	C_6H_6	1 : 1
1a	$CHCl_3$	1 : 0
1b	C_6H_6	1 : 2
1b	$CHCl_3$	1 : 2
1c	$CHCl_3$	1 : 2
1d	$CHCl_3$	1 : 0

solvent was removed at 70—100 °C. As for **1a**, two kinds of samples containing no solvent were prepared: **1a**-I which was obtained by recrystallization from a $CHCl_3$ solution and **1a**-II which was prepared by drying **1a**·C_6H_6 at 70 °C under vacuum. The X-ray diffraction patterns of **1a**-I and **1a**-II were the same, except that some peaks of the latter were a little broadened. This result indicates that these two solids have an identical crystal structure, and that the crystalinity of **1a**-I is probably better than that of **1a**-II. The samples of **1b** and **1c** containing no solvent were obtained by drying of the $CHCl_3$ solvate at 70 °C in vacuo.

Dissociation by Mechanical Energy. When pressure of 400 bar was applied with a press to a solid sample of **1a**—**d** for 5 min, the color of the solid changed from pale yellow to green and an ESR signal appeared. In the cases of **1a** and **1d**, the signal was an almost symmetrical single peak, while the radicals formed from **1b** and **1c** showed an unsymmetrical signal typical for radicals in the polycrystalline solid. An ESR signal with the same line shape appeared on heating of **1a**—**d** in the solid state. Thus, the ESR signal observed on pressing was assigned to **2a**—**d**. The intensity of the ESR signal decreased by about 20% after keeping the sample at room temperature for 1 d, indicating dimerization of the radical was very slow in the solid state. As is seen in Fig. 1, the amount of the generated radicals increased with an increase of the applied pressure. In all the cases of **1a**—**c** the presence of solvent of crystallization significantly reduced the reactivity to dissociation. As for the samples containing no solvent, **1b** and **1c** showed higher reactivity than **1a** and **1d**.

To clarify the origin of the substituent effects, dissociation enthalpies, ΔH_{diss}, for **1a**—**d** were determined in a degassed *p*-xylene solution (Table 2). Since the *p*-substituents on the phenyl rings cause no further steric hindrance in **1b**—**d**, the observed difference in ΔH_{diss} results from the electronic nature of the substituents. According to the MO calculations and hyperfine coupling constants of the ESR signals, the spin

Table 2. Dissociation Enthalpies (ΔH_{diss}/kJ mol^{-1}) of **1a**—**d** in Solution

Compd	This work[a)]	Literature (Solvent)[b)]
1a	96	95 (C_6H_5Cl), 94 (C_6H_6)
1b	89	
1c	86	
1d	92	90 (C_6H_5Cl), 94 (C_6H_6)

a) In *p*-xylene. b) Ref. 15.

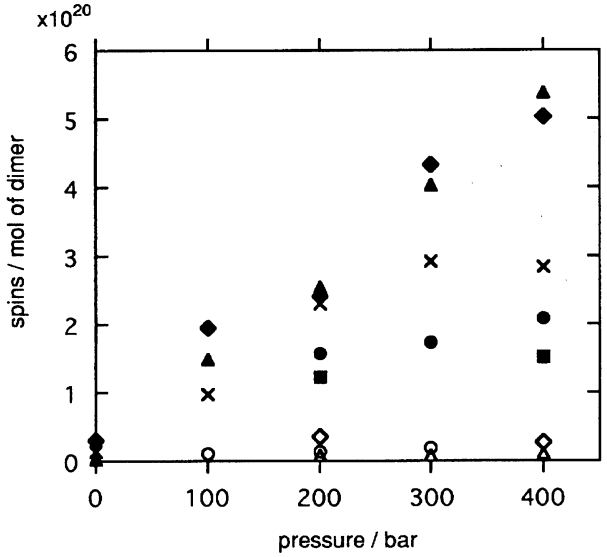


Fig. 1. Plots of the amounts of generated radical per one mole of dimer vs. applied pressure. ●: **1a**-I, ×: **1a**-II, ○: **1a**·C_6H_6, ▲: **1b**, △: **1b**·2C_6H_6, ◆: **1c**, ◇: **1c**·2$CHCl_3$, ■: **1d**.

density was high at the *o*- and *p*-positions of the 2-phenyl rings in radical **2**.[8,9] Therefore, the *p*-substituents can stabilize the radical due to delocalization of the unpaired electron. The higher reactivity of **1b** and **1c** to dissociation by mechanical energy can be attributed, at least partially, to the smaller activation energy required for the bond cleavage. However, the order of the radical yield on the mechanochemical reaction is not same as the order of the ΔH_{diss} value in solution, suggesting that the reactivity under mechanochemical conditions is governed not only by the ΔH_{diss} of the dimer but also by other properties of the solid.

Crystal and Molecular Structures of 1. Do reactive solids such as **1a**—**d** show any anomaly in structural feature, for example, significant elongation of the central bond or very sparse packing with large reaction cavities? Although the structures of the higher reactive neat solids were of greater interest, only **1b**·2$CHCl_3$ and **1b**·2C_6H_6 gave a single crystal suitable for X-ray structure determination. In the former crystal, the molecule **1b** lies on an inversion center and an asymmetric unit consists of a half molecule of **1b** and one molecule of $CHCl_3$. The bond distance (1.576 Å) of C(2)–C(2′) is close to the average value (1.588 Å)[10] of C_{sp^3}–C_{sp^3} distances in hexa-substituted ethanes and much shorter than that (1.624 Å)[5] of the C(3)–C(3′) bond in 3, 3′-bis(5-chloro-3-phenyl-2-benzofuranonyl), which also underwent radical dissociation by mechanical energy. Because a C–S bond is longer than a C–C bond, steric repulsion of **1** will be reduced compared with bis(benzofuranonyl). As is seen in Fig. 2, the phenyl rings at the 2-position are almost perpendicular to the C(2)–C(2′) bond. In the crystal of **1b**·2C_6H_6, **1b** adopts an anti conformation with pseudo-centrosymmetry, but the benzothiophene rings are disordered between two orientations: one site is occupied by an S atom or a C=O group. The C_6H_6 molecule interacts with the *p*-

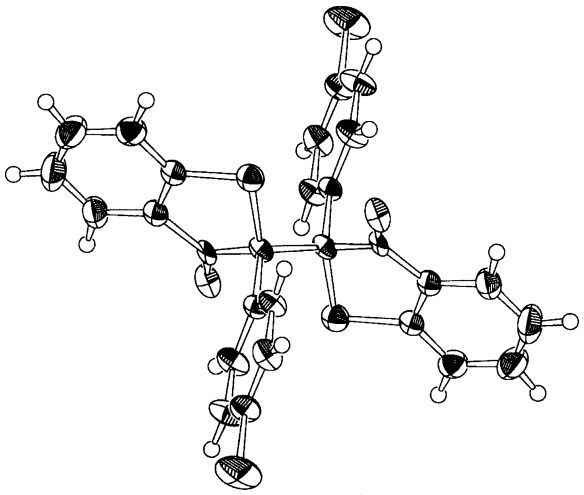


Fig. 2. ORTEP[22] diagram of **1b** in the crystal of **1b**·2$CHCl_3$. The anisotropic thermal ellipsoids enclose 50% probability.

chloro-substituted phenyl group in **1b** through partial π–π stacking. The packing coefficient was 0.70 for **1b**·2$CHCl_3$ and **1b**·2C_6H_6, which is close to the average value for oxohydrocarbons (0.696).[11] The solvent molecules occupy 25 and 29% of the filled volume in **1b**·2$CHCl_3$ and **1b**·2C_6H_6, respectively, suggesting that the solvent of crystallization plays an important role to achieve dense packing.

The crystals examined did not show any anomalous feature which may provide a clue to understand the solid-state reactivity, but dynamic NMR experiments and semi-empirical MO calculations indicated that the molecule of **1** exists mainly as a different conformer in solution from that observed in the crystal. In the spectrum of **1d** in CD_2Cl_2 measured at 228 K, three singlet signals assigned to the methoxy protons were observed at δ=3.84, 3.82, and 3.70 with a ratio of 10 : 10 : 1. When the temperature raised, the former two singlets coalesced at ca. 298 K and the latter signal was broadened. This dynamic behavior corresponds to restricted rotation around the central C–C bond.[12] The major rotamer was assigned to a gauche form based on the nonequivalence of the tow methoxy groups, while the minor one was the centrosymmetric anti form. As for **1a—c** the signals were rather broad in $CDCl_3$ at room temperature and sharpened on decreasing temperature, indicating occurrence of the same type of restricted rotation.

PM3[13] calculations were done for **1a** and **1b** with structure optimization. As for the anti form, the optimized structure was closely almost the same as that observed in the crystal of **1b**·2$CHCl_3$. The heats of formation (ΔH_f) of the gauche forms were lower than those of the anti forms by 20.5 and 20.3 kJ mol^{-1} for **1a** and **1b**, respectively. Although these values of $\Delta\Delta H$ were much larger than the difference in free energy $\Delta\Delta G°$ (5.7 kJ mol^{-1}) obtained for **1d** at 228 K, the relative stability agreed with the experimental results. The existence of the less stable anti conformer in the crystal might result from intermolecular forces.

Energy Transport in the Solid. In order to understand reactions induced by mechanical energy, the flow of energy in the solid should be considered. Dlott and Fayer[14] reported an analytical theory for the shock-induced chemical reaction of organic solids. According to their calculations, when a shock such as a sudden change of external pressure is applied to a molecular solid, the mechanical energy is first deposited in the acoustic phonon modes followed by equilibration with the optical phonon modes. Then two or more excited phonons transfer the excess mechanical energy to an internal vibration of the molecule constituting the solid through anharmonic interaction with the molecular vibration. Once a certain mode of vibration is excited, the bond which is potentially cleaved can be activated by a fast intramolecular vibrational redistribution process. In the present case, although the applied pressure (<400 bar) is much smaller than their model (20 kbar), a similar flow of energy will occur in the compressed solid, and as a result, a molecular vibration will be excited. Although **1a**-I and **1a**-II had the same crystal structure, the latter showed somewhat higher reactivity to dissociation than the former. Since **1a**-II, which was obtained as powder by drying the crystals of **1a**·C_6H_6, probably contained more defects than **1a**-I, the observed difference in reactivity suggests that the dissociation reaction may be enhanced by the presence of defects, as was pointed out by Fayer et al.[15]

At the present stage, the reason of the decrease in reactivity by the presence of solvent of crystallization is not clear. The TG-DTA curves of the compressed sample indicated that the solvent of crystallization still remained after applying pressure. Considering the larger amplitudes of thermal vibrations in the solvent molecule compared with those in the substrate molecule (shown by the X-ray study for **1b**), the applied mechanical energy might be consumed by vibrational motion of the solvent molecules rather than by the reaction of **1**, to result in lower reactivity to dissociation in comparison with solids containing no solvent.

Experimental

IR spectra were taken on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a JEOL GSX-400 or GSX-270 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-DX303 mass spectrometer by CI method using NH_3 gas. ESR spectra were recorded on a JEOL JES-FE2XG spectrometer equipped with a temperature control unit. Decomposition points were obtained from TG-DTA curves recorded on a Shimadzu DTG-50 under N_2 atmosphere. X-Ray diffraction patterns for the powdery samples were recorded using Cu $K\alpha$ radiation with the scan speed of 2 °min^{-1} for the 2θ range of 4—35°.

Materials. 2,2′-Bis(2-aryl-3-benzothiophenonyl)s **1a—d** were prepared by the methods of Kalb and Bayer[7] with some modifications and were recrystallized from C_6H_6 or $CHCl_3$. Since elemental analysis is not useful to detect contamination of the monomer precursor, 2-aryl-3-benzothiophenone, purities of **1a—d** were checked by TLC on silica gel (Merck, Kieselgel 60 F_{254}) and ^{1}H NMR spectra. In the spectra of **1a—d** there was no signal assigned to the 2-H of the corresponding monomer, which appeared at δ=5.3—5.4 as a singlet.

***meso*-2,2′-Bis(2-phenyl-3-benzo[*b*]thiophenonyl) (1a).** Mp 227—228 °C (decomp, lit,[7] 231 °C); IR (KBr) 1690, 1585, 1490,

1455, 1285, 1080, 760, 740, 705, and 683 cm^{-1}; ^1H NMR (270 MHz, in $CDCl_3$, −20 °C) δ=7.01 (d) and 7.2—7.9 (m); MS *m/z* 451 (M^++1).

***meso*-2,2′-Bis[2-(4-chlorophenyl)-3-benzo[*b*]thiophenonyl)] (1b).** Mp 212 °C (decomp); IR (KBr) 1693, 1586, 1493, 1449, 1400, 1285, 1219, 1015, 831, 820, 779, 760, and 737 cm^{-1}; ^1H NMR (400 MHz, in CD_2Cl_2, −50 °C) δ=6.88 (d) and 7.1—7.8 (m); MS *m/z* 518, 520, and 522 (M^+).

***meso*-2,2′-Bis[2-(4-bromophenyl)-3-benzo[*b*]thiophenonyl)] (1c).** Mp 184 °C (decomp); IR (KBr) 1690, 1585, 1485, 1450, 1397, 1283, 1010, 793, and 737 cm^{-1}; MS *m/z* 606, 608, and 610 (M^+).

***meso*-2,2′-Bis[2-(4-methoxyphenyl)-3-benzo[*b*]thiophenonyl)] (1d).** Mp 215 °C (decomp, lit,[16] 210 °C); IR (KBr) 1695, 1606, 1587, 1508, 1450, 1256, 1189, 1033, 835, 796, and 755 cm^{-1}; ^1H NMR (400 MHz, in $CDCl_3$, −30 °C) δ=3.70, 3.82, 3.84 (each s, OMe), 6.75 (d, *J*=9 Hz), 6.81 (d, *J*=9 Hz), 7.00 (d, *J*=9 Hz), 7.2—7.6 (m), 7.75 (d, *J*=8 Hz), and 7.83 (d, *J*=8 Hz).

Determination of Dissociation Enthalpies in Solution. A sample solution of **1a**—**d** in *p*-xylene (5×10^{-4} mol dm^{-3}) was degassed and the ESR spectra were recorded at various temperatures between 20 and 130 °C. The concentration of the radical was determined using a degassed *p*-xylene solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) as standard.

Determination of the Degree of Dissociation by Mechanical Energy. The powdered sample (20 mg) was placed in a KBr disk maker (10 mm ϕ) and pressure was applied with a press for 5 min. The pressed sample was broken up into several pieces, weighed, and transferred into an ESR cell, and the ESR spectrum was immediately recorded at 22 °C. The number of spins was determined using a freshly prepared benzene solution of TEMPOL as standard. The Mn marker was used for correction of the sensitivity.

X-Ray Structure Analysis of 1b·2CHCl$_3$ and 1b·2C$_6$H$_6$. Data collection was performed on a Rigaku AFC-7R four-circle diffractometer with monochromated Cu $K\alpha$ radiation using 2θ–ω scan technique at 25 °C. Three standard reflections were monitored every 150 reflections. For **1b**·2$CHCl_3$, the intensities gradually decreased by ca. 5%, and correction for decay was applied. Absorption was corrected by Ψ-scan. The structures were solved by direct methods with SHELXS86.[17] For **1b**·2$CHCl_3$, full-matrix least-squares refinement was carried out on *F* using TEXSAN system[18] with anisotropic thermal parameters for non-H atoms, and H-atoms were located on difference maps and refined isotropically. The occupancy factors of the disordered Cl atoms in $CHCl_3$ were fixed to 0.9 and 0.1. In the case of **1b**·2C_6H_6, refinements were done on F^2 using SHELXL93.[19] The disordered atoms were refined isotropically with geometrical constraints and their occupancy factors were fixed to 0.5, so that the temperature factors were almost equal for the corresponding atoms. All the H-atoms of **1b** were included using a riding model. Crystal data and details for data

Table 3. Crystal Data and Details of Data Collection and Structure Determination

Compd	**1b** · 2$CHCl_3$	**1b** · 2C_6H_6
Formula	$C_{28}H_{16}Cl_2O_2S_2$·2 ($CHCl_3$)	$C_{28}H_{16}Cl_2O_2S_2$·2 (C_6H_6)
F.W.	758.2	675.6
Crystal size /mm	0.4×0.3×0.2	0.4×0.4×0.2
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	17.745(3)	9.997(2)
b/Å	9.937(3)	10.092(2)
c/Å	9.057(1)	9.130(2)
α/°		82.91(2)
β/°	90.21(1)	114.09(2)
γ/°		93.65(2)
V/Å^3	1600.1(4)	834.4(3)
Z	2	1
D_x/g cm^{-3}	1.574	1.345
λ/Å	1.5418	1.5418
μ/cm^{-1}	79.0	31.9
F(000)	764.0	350.0
Scan width/°	1.84+0.4tan θ	1.1+0.15tan θ
Scan speed/° min^{-1}	8 (θ)	8 (θ)
$2\theta_{max}$	120.0	130.0
No. of reflections		
measured	2714	2999
unique	2537	2999
observed	2057	2607
Criteria for obsd	$I_o>3\sigma(I_o)$	$F_o>2\sigma(F_o)$
$(\Delta/\sigma)_{max}$	0.29	1.07
$\Delta\rho_{min}$, $\Delta\rho_{max}$/Å^{-3}	−0.70, 0.53	−0.45, 0.52
No. of parameters	234	346
R	0.067	0.083[a]
wR	0.053	0.237[b]
S	7.94	0.963
Weighting scheme	$1/\sigma^2$	$[\sigma^2(F_o^2)+(0.1723p)^2+1.18p]^{-1}$ [c]

a) for $F_o>4\sigma(F_o)$. b) $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. c) $p=0.66667\times F_c^2$.

collection and refinements are listed in Table 3.[20]

Calculations. Semi-empirical MO calculations were carried out with the program MOPAC ver. 6.01.[21] As for the anti form, the structure determined by X-ray study was used as the initial structure and optimized under C_i symmetry. Packing coefficients were calculated by the program OPEC[22] for the observed crystal structures.

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