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Consequences of molecular strain on the solid state addition reaction

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An overview is given on the solid-state addition reaction under mechanical stressing. Enhanced charge transfer across the boundary of dissimilar chemical species was observed mainly in terms of local polarization and/or radical formation. Associated anomaly of electron distribution is regarded mainly as a consequence of broken symmetry at various levels, i.e. molecular orbitals, crystal fields or ligand fields. A new preparation method of some ferrous coordination compounds is demonstrated. Recent preliminary results on some organic addition reactions are then displayed. Mechanisms of organic adduct formation via a series of Diels-Alder reactions are speculated. Outlook towards a new possibility of mechanochemical reactions in the direction of organic synthesis are also given. © *2004 Kluwer Academic Publishers*

1. Introduction

A solid state addition reaction begins by charge transfer across the boundary of dissimilar solids. This is generally enhanced by local polarization. Unusual electron distribution is a consequence of the strained bonds since the bond strain is accompanied by a loss of molecular symmetry. Symmetry of molecules is associated with the basic nature of electron orbitals and hence predominated by respective wave functions. It is, therefore, natural to conceive that the symmetry is specific to the compound. This is correct, as far as we talk about free molecules. In a crystal, however, plastic deformation brings about local loss of the symmetry of crystal fields or ligand fields. This in turn changes the Madelung potential and hence local ionicity in the case of ionic crystals. In the case of molecular crystals, each molecule occupying the lattice site can be irreversibly deformed to destroy symmetry of their electron distribution. We cannot overemphasize that strained molecular states are only sustainable in a solid state.

In the previous symposium held in Novosibirsk (International Conference Fundamental Bases of Mechanochemical Technologies, Aug. 2001) the author has discussed about the distribution of ligand field strength as a consequence of mechanical stressing [1]. The present overview develops the idea into wider range towards organic synthesis. While new style of the mechanochemical synthesis of coordination compounds is established by combining mechanical stressing and annealing to obtain unusual complex compounds, we further proceed to synthesize organic compounds without any participation of metallic species. Apart from spin crossover mentioned in Ref. [1], formation of radicals is often regarded as a consequence of symmetry loss of the electron distribution. When we observe aromatic compounds with rich π-bonds, dearomatization results in the radical formation due to $\pi \rightarrow \sigma$ state change of the electron. This is associated with the change in the carbon electronic states between SP2 and SP3. The latter part of this overview is, therefore, dedicated to the mechanochemical organic synthesis involving aromatic compounds. Recent experimental results on the mechanochemical Diels-Alder reactions between some derivatives of anthracene and *p*-benzoquinone or fullerene are presented. Some preliminary computational results are also discussed.

2. Formation of new coordination compounds

When a mechanical stress is exerted on coordination compounds in a solid state, their constituent molecules are subject to distortion. The distortion, in turn, causes a change in the magnitude and anisotropy of the ligand field. Such changes in the ligand field lead to a considerable modification of magnetism and reactivity [2–7]. In our previous studies, we found that the milling of iron(II) complexes with 1,10-phenanthroline gave rise to loss of crystallinity and reduction of ligand field symmetry [2–5]. As we tried to anneal the mechanochemical products at temperatures well below those for decomposition or melting, crystalline states were restored close to or identical with the intact crystals synthesized in a liquid state. However, the loss and restoration of the crystallinity do not always parallel their magnetic properties in a reversible manner. The relationship between the crystallinity and the magnetic properties of the coordination compound, $[Fe^{II}(phen)_3](PF_6)_2$, is therefore discussed in view of the properties control by combining mechanical stressing and thermal relaxation [8].

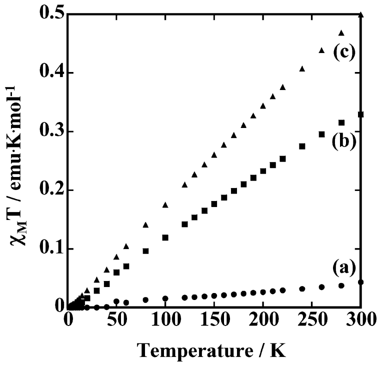

Figure 1 Temperature dependence of observed values of $\chi_M T$ for $[Fe(phen)_3](PF_6)_2$; (a) intact, (b) after milling for 5 h, (c) annealed at 473 K after milling for 5 h.

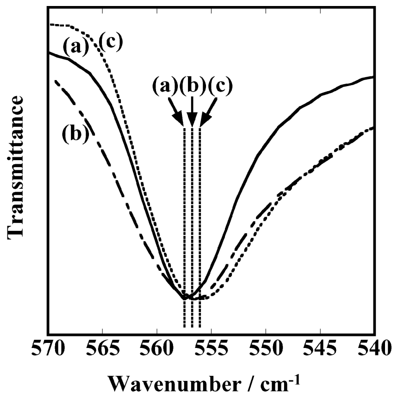

Figure 3 Mid-infrared absorption spectra of $[Fe(phen)_3](PF_6)_2$; (a) intact, (b) after milling for 5 h, (c) annealed at 473 K after milling for 5 h.

As shown in Fig. 1 by curve (a), the intact $[Fe(phen)_3](PF_6)_2$ exhibits very small value of $\chi_M T$ due to its diamagnetism. The value of $\chi_M T$ for $[Fe(phen)_3](PF_6)_2$ after milling by a planetary mill for 5 h increases quasi-linearly without any sharp increase, as shown by curve (b). The change in $\chi_M T$ is attributed to a widened distribution of the ligand field strength by milling [4]. One of the most remarkable features of the change in $\chi_M T$ is its further increase by subsequent annealing at 473 K (curve (c)).

Milling of $[Fe(phen)_3](PF_6)_2$ for 5 h brought about almost complete amorphization, as shown in Fig. 2 by the curve (b). Recrystallization by subsequent annealing was obvious (curve (c)). When the magnetic property is predominated by the long-range order of the molecules, we may expect the decrease in $\chi_M T$, since we observe the restoration of its crystallinity very close to that of the intact specimen by annealing. Therefore, the irreversible change in the magnetic properties shown in Fig. 1 cannot be explained by the crystallographical properties or associated long-range ordering.

As we observed far infrared spectrum, the annealed sample exhibits the recovery to its intact state. It is therefore obvious, that the irreversible change of the magnetic properties shown in Fig. 1 cannot be associated with the strain of the complex ion either. We did not observe any peaks due to impurity or decomposed products. This result is compatible with the magnetic behavior at low-temperature, i.e., without any jump of $\chi_M T$. We found, however, the change in the state of counterion, PF_6^-, to be quite different from those of the complex ion. As shown in Fig. 3, the absorption band due to PF_6^- shifted toward low wavenumber side by 1 cm^{-1} with simultaneous broadening, as shown by the curves (a) and (b). By annealing, further decrease in the wavenumber by 1 cm^{-1} and the wider half width compared to intact sample was observed (curve (c)).

Another irreversible change by annealing is observed from the UV-VIS spectra shown in Fig. 4. The absorption band due to $\pi^* \leftarrow \pi$ transition at around 295 nm (curve a) shifted toward higher wavelength by ca 30 nm by milling (curve b). The peak further shifted in the same direction by subsequent annealing as well by 10 nm (curve c), with simultaneous peak broadening. By annealing the milled products, the amorphous state was relaxed by recrystallization. Most of the counterions, PF_6^-, were packed in a state with higher spherical symmetry, unlike intact $[Fe(phen)_3](PF_6)_2$ crystallized in a solution. This difference in the packing state might be attributed to the difference of the molecular mobility between the liquid and solid states. Because of the smaller mobility of PF_6^- in the solid state, recrystallization can progress without redistortion of PF_6^-. Restoration of the strain of the counterion disturbs the structural stabilization by π-π stacking. In other words,

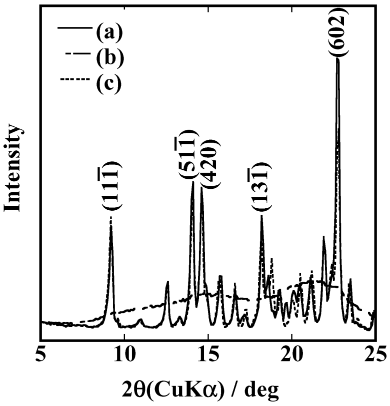

Figure 2 XRD profiles of $[Fe(phen)_3](PF_6)_2$; (a) intact, (b) after milling for 5 h, (c) annealed at 473 K after milling for 5 h.

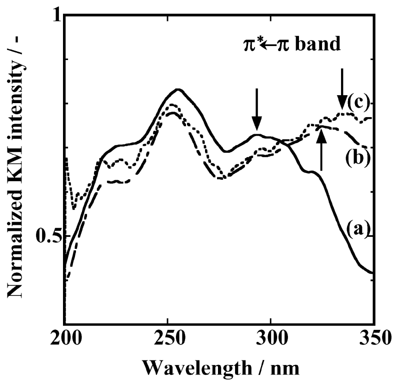

Figure 4 UV-VIS diffuse reflectance spectra of $[Fe(phen)_3](PF_6)_2$; (a) intact, (b) after milling for 5 h, (c) annealed at 473 K after milling for 5 h.

restoration of the spherical symmetry of PF_6^- counterions induces an increase in the free volume and delocalization of electron density around a phen ring. This reduces the ligand field strength and, hence, increases the effective magnetic moment. Thus, it is well possible to obtain some coordination compounds with anomalous magnetic properties by combining a preliminary mechanochemical reaction with subsequent annealing. We also found similar possibility in a series of oxalate complexes [9].

3. Mechanochemical Diels-Alder reaction

A Diels-Alder reaction, one of the most popular organic name-reactions, produces two new carbon-carbon bonds to form six-membered carbon skeletons from a reaction mixture comprising a diene and a dienophile species. Diels-Alder reactions become generally more feasible when the dienophile bears electron-withdrawing groups and the diene electron-donating groups. The reaction is highly stereospecific and the orientation of the groups on the dienophile is retained in the product. It is therefore challenging to explore application of mechanochemical Diels-Alder reaction to this kind of organic synthesis. Some attempts were reported to obtain adducts under the influence of photon irradiation [10, 11] or heating under microwave [12, 13]. A preliminary attempt of grinding was also reported [14]. However, little discussion was made on the reaction mechanisms. In our laboratory, we have conducted experimental studies on the mechanochemical reactions between anthracene derivatives and either *p*-Benzoquinone or fullerene. Preliminary results are given below to stimulate constructive discussion.

3.1. With *p*-benzoquinone [15]

A mixture of *p*-benzoquinone (54.05 mg or 0.5 mmol) and an equal molar amount of anthracene derivatives was subjected to mechanochemical reaction by a small electromagnetic vibro-mill (Fritsch Vibratory Micro-Mill, Pulverisette 0) with a stainless steel or agate vial with a single milling ball of the same material, at 50 Hz (3000 rpm) in frequency and 2 mm in amplitude. Reaction yield was estimated by ^{1}H NMR (CDCl3) (Varian Mercury-300). EPR spectra were obtained by an EPR spectrometer (Jeol JES-RE3X) on the solid sample in an amount, 50 mg. Spin concentration was determined by comparing with Benzene solution of 2,2,6,6-Tetramethyl-1-piperidinyloxy free radical (TEMPOL).

As we milled mixtures comprising some derivatives of anthracene and *p*-benzoquinone (PBQ), we observed appreciable mechanochemical reaction, as shown in Table I [15]. Increasing yield in the order from anthracene, 9-methyl to 9,10-dimethylanthracene is expected from ordinary sense of organic chemistry, just because of the electron donating properties of methyl groups. We then examined the change in the spin concentration upon milling individual reactant or the reaction mixture for the system, 9,10-dimethylanthracene (DMA) and PBQ. The spin concentration significantly increased by vibro-milling, either a single component or a mixture. As shown in Table II, the increase in the spin concentration by milling is more significant on DMA than on PBQ. The increase in the spin concentration upon milling a DMA-PBQ mixture is also significant and slightly more than the average for DMA and PBQ. It is not possible to determine, at this stage, to what extent radicals were consumed during reaction.

TABLE I Reaction yield of mechanochemical reactions between *p*-benzoquinone and anthracene derivates after milling for 5 h. See text for experimental details

Diene	Yield/%
Anthracene	0
9-methylanthracene	5
9,10,dimethylanthracene	73

The role of the radicals for the present mechanochemical Diels-Alder reaction is not fully elucidated yet. In a study on the same reaction system via a conventional solution route, Fukuzumi and Okamoto has discussed the catalytic activity of Mg^{2+} on the rate of electron transfer from DMA to PBQ, after confirming this single electron transfer being rate determining [16]. In a solid state without any catalysis, formation of radicals by milling a single species seems to be a consequence of the change in the intramolecular configuration. It is therefore reasonable to speculate at this stage that the electron transfer necessary for the adduct formation is assisted by the formation of radicals.

Note that the mechanochemical reaction by milling with the vial and ball of stainless steel is faster than with those of agate. However, the reaction with agate parts is still quite obvious. Therefore, the catalytic effects of transition metals from vials and balls during milling cannot be predominant, if subsidiary. The apparent dependence of the reaction rate on the material of vial and ball is rather associated with the difference in the density and accordingly in the intensity of single impact. Mechanisms of the present mechanochemical addition reaction will further be discussed on the next chapter where we discuss the computational results.

3.2. With fullerene [17]

A mixture of fullerene (C_{60}) (144 mg, 0.2 mmol) and an equal molar amount of DMA was milled together with vibratory mill as in the case of the reaction with

TABLE II Change in the radical concentration by milling. See text for experimental details

Compounds	Milling time/h	Counted spin ($\times 10^{13}$)	*g*-value	Relative number of spins per molecule[a]
Dimethyl anthracene	0	8.8	2.0036	1.0
Dimethyl anthracene	5	43.1	2.0041	4.9
p-benzoquinone	0	5.3	2.0036	1.0
p-benzoquinone	5	6.8	2.0043	1.3
Dimethyl anthracene + *p*-benzoquinone	5	24.1	2.0038	3.4[a]

[a]Compared with the average value of the intact reactants.

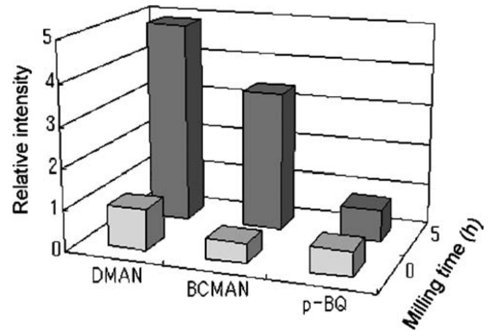

Figure 5 Change in the relative spin intensity by milling aromatic compounds. DMAN: 9,10-dimethylanthracene; BCMAN: 9,10-bis(chloromethyl)anthracene; *p*-BQ: *p*-benzoquinone [15].

TABLE III Change in the radical concentration by milling. See text for experimental details

Compounds	Milling time/h	Counted spin	*g*-value	Relative number of spins per molecule[a]
Fullerene	0	6.9×10^{13}	2.0023	1
Fullerene	5	1.3×10^{17}	2.0023	185
Fullerene	5[a]	5.0×10^{16}	2.0023	72
Fullerene	5 (in N_2)	2.9×10^{16}	2.0023	41
Fullerene	5 (in N_2)[b]	4.1×10^{15}	2.0025	6
Dimethyl anthracene	0	8.8×10^{13}	2.0036	1
Dimethyl anthracene	5	4.3×10^{14}	2.0041	5
Fullerene + Dimethyl anthracene	0	6.4×10^{14}	2.0029	1
Fullerene + Dimethyl anthracene	5	5.3×10^{15}	2.0027	8.3

[a] After evacuation for 45 min.

[b] After dissolving into CS_2 and vacuum dried for 1 h.

PBQ. The yield and conversion were determined by ^1H NMR ($CDCl_3$-CS_2 1:1).

Changes in the conversion and yield, determined from the concentration of DMA and the principal product, mono adduct of DMA and C_{60}, respectively, are shown in Fig. 6 [15]. Discrepancy between two quantities is attributed to the formation of the side products, bis or tris adduct of DMA and C_{60}. The yield under the same condition between DMA and PBQ after milling for 5 h was 14.1%, so that higher mechanochemical reactivity of C_{60} than PBQ was obvious. Change in the spin concentration was observed under various milling conditions. As shown in Table III, the radical concentration increases by up to two orders of magnitude upon milling fullerene. The increase is much larger than in the case of milling anthracene derivatives. Since it is known that coexistence of oxygen increases the paramagnetic species, we also tried to eliminate adsorbed gaseous species by vacuum drying or to mill in nitrogen atmosphere. The reduction of spin concentration by evacuation is significant but limited. Increase in the spin concentration after milling in N_2 is much smaller but is still significant. We therefore think that the increase in the radical concentration by milling cannot mainly be attributed to the reaction with oxygen.

On the other hand, we observed that the radical concentration of milled fullerene dramatically decreased after partial dissolution into CS_2 and recrystallization. It is therefore natural to assume, that most of the radical species are accommodated in fullerene in a solid state. On the other hand, the radical concentration did not decrease significantly upon annealing at 200°C for 4 h. This implies unusually stable paramagnetic states in milled fullerene. Although there are still many unsolved puzzles, we may safely state that mechanical activation results in a very unusual spin states of C_{60}.

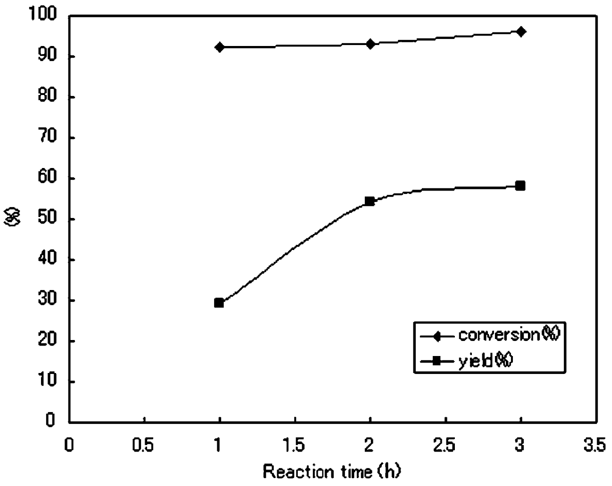

Figure 6 Change in the conversion and yield with milling time for the system, 9,10-dimethylanthracene and fullerene.

Upon milling a mixture of fullerene and DMA, we observed a significant increase in the spin concentration. The extent of increase was, however, much smaller than the case of milling fullerene alone. This implies that radicals are consumed by reacting with DMA. We have to bear in mind that in a milling vial, there is always a wide varieties of the states, i.e., different states of activation in the unreacted species, i.e., C_{60} and DMA, as well as the products with varying states of reaction. It is known that some of the Diels-Alder reaction occurs by forming two new bonds at the same time. As mentioned previously in conjunction with the reported effect of Mg^{2+} as a catalyst [16], however, a single electron process and a stepwise formation of two bonds is much more likely. It is even likelier in the case of mechanochemical reaction, since the reaction has basically stochastic in nature. Participation of radicals or spins is in line with the stepwise mechanism mentioned above. Much smaller amount of increase in the spin concentration by milling a mixture may be attributed to the consumption of radicals by mechanochemical reaction. The difference in the spin increase by milling between single component and the mixture is much more appreciable for the systems involving C_{60} than those with PBQ. This is in line with the faster reaction rate for the former system than the latter.

It is noteworthy that the radical concentration in fullerene even after milling for 5 h was still only 2.7×10^3 spins/molecule, while the conversion was close to completion after milling for 3 h. This might be explained when we postulate that the charge transfer process, being indispensable for any

Diels-Alder reactions, induces further radical formation by a reaction-induced strain. Repetition of such a series of processes can proceed like a chain reaction.

Bettinger *et al.* referred radical formation mechanisms in conjunction with the Stone–Wales transformation (SWT) of fullerene [18]. They discussed SWT in their study on the mechanical strength of carbon nanotube. As a species of activated complex in the course of SWT, a concerted rotation of a C2 unit exhibits a diradical. They pointed out the formation of diradicals upon tensile stressing. The process is much better defined than what is happening during mechanochemical reaction. It is, however, well conceivable, that the formation of radicals by milling fullerene is more or less similar to this kind of process. Irreversible formation of long-lived radicals needs further explanation. This could be associated with mechanochemical dearomatization. This will further be discussed below.

4. Computational study on Diels-Alder reaction

The accepted reaction mechanism a Diels-Alder reaction involves the process in which reactants approach with each other in a manner where the principal planes of each reactant are canted just for the new bonds to form as a result of the overlap of π-electrons clouds [19]. In the case of reactions by free molecules, it is known that the dihedral angle of anthracene decreases from 180° to the minimum 150° as the distance to PBQ is reduced to form an activated complex, as illustrated in Fig. 7.

In a molecular crystal under mechanical stressing, constituent molecules are distorted. It is natural, then, to postulate that those molecules whose strain is close to the favorable state to form activated complex are apt to react even without acquiring activation energy in the form of thermal vibration. Otherwise states, some distorted reactant molecules are apt to transfer charges "spontaneously".

It is well known that the HOMO-LUMO gap (HLG) between the two reactant molecules serves as a criterion of the reaction feasibility. Aihara proposed the concept of reduced HLG as a criterion of kinetic stability of polycyclic aromatic hydrocarbons [20]. In the present case of Diels-Alder reaction, the reaction feasibility depends on the relationship between the diene's highest occupied molecular orbital (HOMO) and the dienophile's lowest unoccupied molecular orbital (LUMO), i.e. between anthracene derivatives and PBQ. We have calculated the HLG as a function of dihedral angle of the central benzene ring in anthracene. As shown in Fig. 8, HLG decreases with decreasing dihedral angle. When the central benzene ring bends, the kinetic stability of anthracene toward reaction with PBQ decreases and the reactivity for the Diels-Alder reaction correspondingly increases. This kind of primitive calculation favors, at least qualitatively, a mechanochemical reaction due to molecular strain.

We further calculated the variation of HLG as a function of dihedral angle for derivatives of anthracene. As shown in Fig. 9, the tendency of decreasing HLG with decreasing dihedral angle is alike for all the derivatives. It is particularly interesting to note that the value of HLG at the same dihedral angle is the

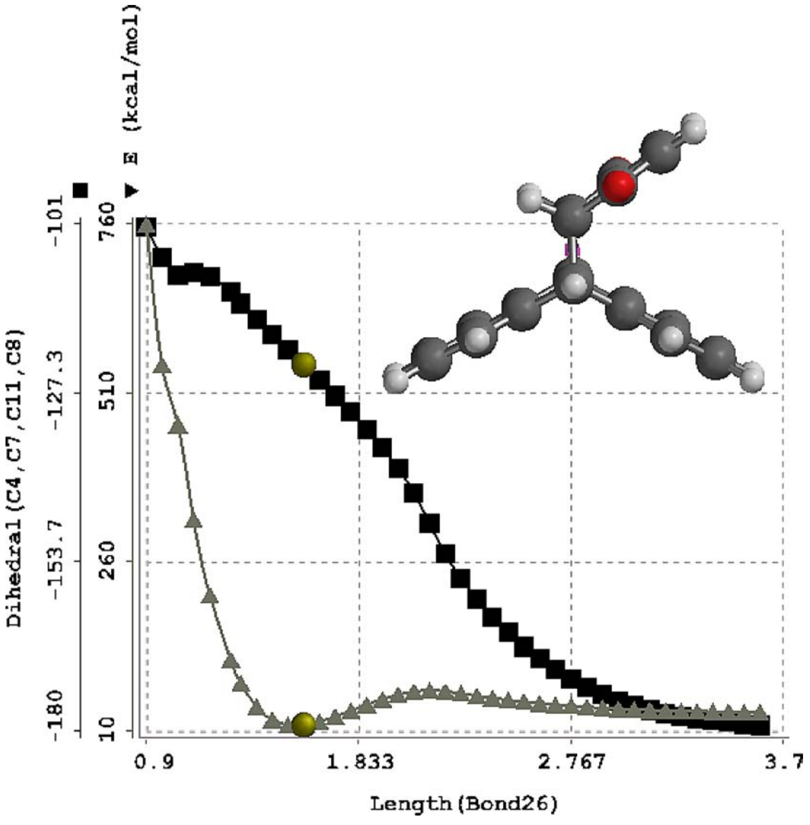

Figure 7 Change in the dihedral angle of anthracene (square) and the total energy (triangle) with the intermolecular distance for the system anthracene and : p-benzoquinone.

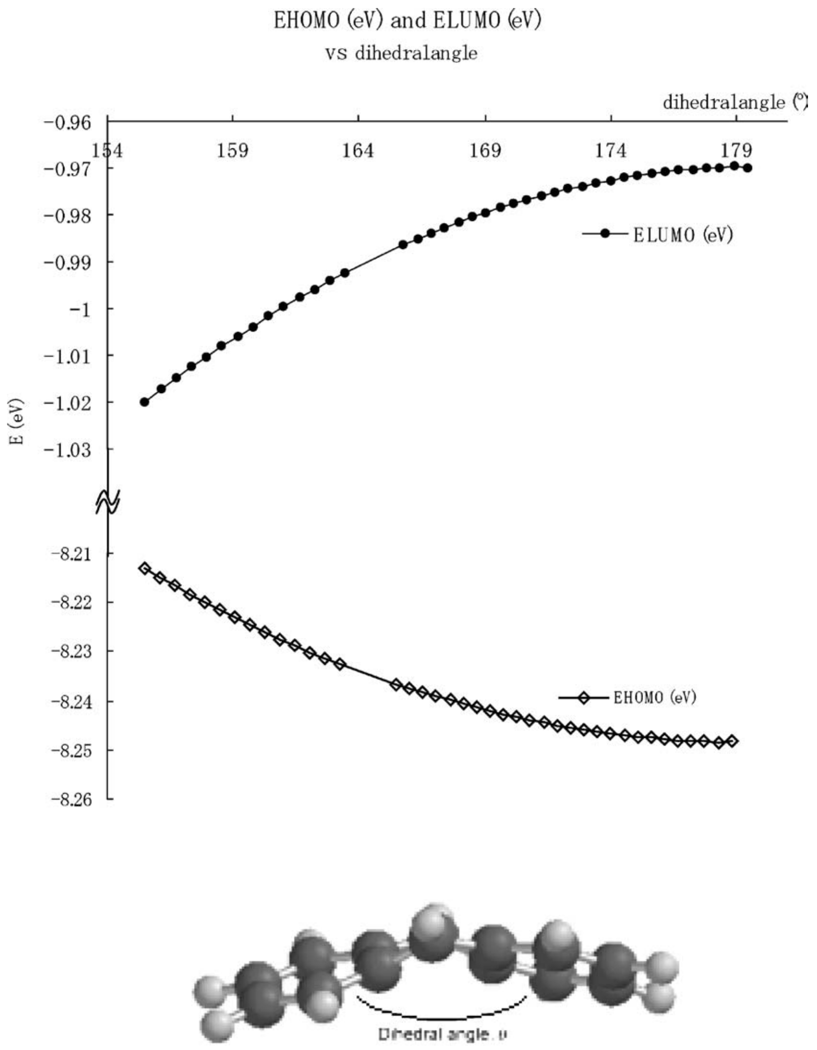

Figure 8 Change in the HOMO and LUMO with the dihedral angle of anthracene.

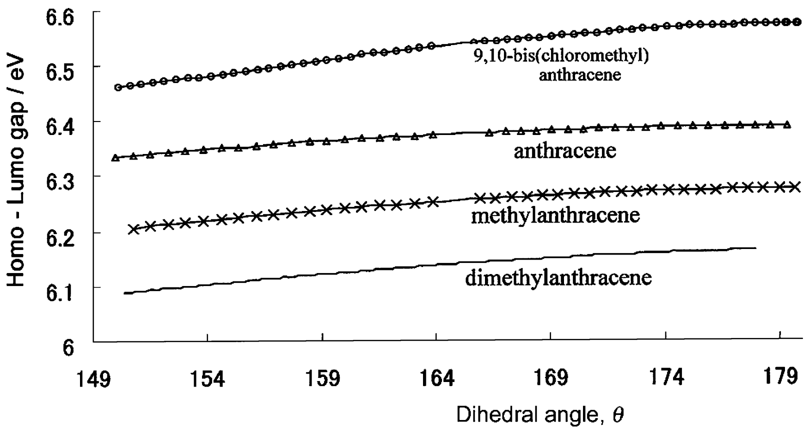

Figure 9 Change in the HOMO–LUMO gap with the dihedral angle of anthracene and its derivatives.

smallest of all the derivatives for dimethyl anthracene. This is coincides with the experimental results shown in Table I, although the variation of the molecular weight or the number of carbon atoms is not taken into account.

The present computational results and associated discussion contains many problems yet to be solved. One is the accuracy of computation based on the semi-empirical method. This seems to be risky, particularly because of the participation of radicals. As discussed in conjunction with the results shown in Tables II and III, radicals seem to play one of the key roles in our reaction system. As for the interpretation of HLG, we may not straightforwardly connect the results with the reaction feasibility. As stated in Refs. [19] and [20]. HLG by itself cannot always be an exact measure of the kinetic stability of the compounds. Correction for the quantity and quality of carbon atoms involved should be taken into account. Change in the HLG as a function of dihedral angle, as shown in Fig. 8 may at least qualitatively be reliable, since in this case, we observe only one molecular species.

In spite of all the difficulties and incompleteness, the author believes the significant role of molecular strain and associated radicals in the organic mechanochemical reactions. The decrease in the HLG with decreasing dihedral angle, shown in Fig. 8, might favor, if partly, the idea, since the tendency is at least qualitatively correct, however inaccurate the computational results might be.

5. Summary and outlook

Mechanical activation and mechanochemical reactions, basically developed to better utilize natural resources, and hence almost exclusively dedicated to the field of inorganic chemical fields, can well be extended to the empire of organic syntheses. Examples were given for two different fields, i.e., to the syntheses of transition metal coordination compounds and organic synthesis by Diels-Alder reaction. Common feature is the utilization of the consequences of unusual electronic states due to irreversible breakage of symmetry at various levels. Some very primitive speculation based on the semi-empirical computational results was given to stimulate discussion. The discussions given above are still premature. Nevertheless, grand design of mechanochemistry for organic synthesis will have a bright future. It is a challenge against the symmetry of the wave function, and is certainly more than an illusion, since we have many evidences, however indirect they are.

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