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First kinetic evidence for the CH/π and π/π solute–solvent interaction of C_{60} in the Diels–Alder reaction with cyclohexadiene†

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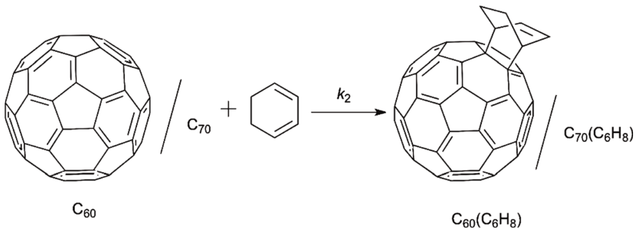
The first CH/π solute–solvent interaction of C_{60} was evidenced by the kinetic solvent effects in the Diels–Alder reaction with 1,3-cyclohexadiene based on the evaluation of linear free energy relationship of log k_2 with empirical solvent polarity and basicity parameters, $E_T(30)$ and D_π, respectively.

Due to its spherical molecular structure and highly conjugated double-bond system, C_{60} fullerene has received much attention with respect to its physicochemical properties as well as its synthetic applications in biological and materials science.[1] Mostly, chemical modifications and functionalizations are carried out in organic solvents and thus the solution behavior of C_{60} will provide useful information on selecting solvents for practical processing. There are some studies concerning the interaction of C_{60} with solvent molecules, *e.g.*, the solubility in organic solvents[2] and the spectroscopic and thermodynamic analyses of solvent complexation.[3] Of further interest is the formation of C_{60} solvates (or clathrates) with alkanes,[4] halogenated alkanes,[4c,5] benzenes[6] and halobenzenes.[7] These solvent molecules are intercalated between the bulky C_{60} balls. Nishio *et al.*[8] searched the Cambridge Crystallographic Database and disclosed that weak forces, such as CH/π interactions, play vital roles in deciding the solid structures of C_{60} complexes. However, little is known about the solvation effects on the dynamic chemical reactions of C_{60} probably because of poor solubility in common solvents. Therefore, a systematic study of the kinetic solvent effects is needed to give an insight into the solute–solvent interaction of C_{60} in the initial state as well as the solvation of transition state.[9]

Recently, we have reported that the rate of 1,3-dipolar cycloaddition of diazodiphenylmethane (DDM) with C_{60} in various solvents has a tendency to increase with increasing solvent polarity but decrease with increasing solvent basicity.[10] This cycloaddition seems to be insufficient to evaluate the specific solute–solvent interaction of C_{60} due to the intervention of solvation of a possible polar transition state (as indicated by the Hammett's ρ value of −1.6). This situation prompted us to choose an ideal C_{60} reaction *via* a less polar transition state[11] and explore the initial state solvation of C_{60}. In this paper, we wish to report the kinetic solvent effects on the Diels–Alder (DA) reaction of C_{60}/C_{70} with 1,3-cyclohexadiene (Scheme 1)[12] and disclose the CH/π and π/π interactions of C_{60} on the basis of the linear free energy relationship of log k_2 with solvent polarity and basicity parameters.

The kinetic measurements for the DA reaction of C_{60} and C_{70} with cyclohexadiene were performed under pseudo-first order conditions in various solvents at 30 °C by using a large excess of diene (>50 equiv) relative to fullerenes (1.0×10^{-5}–10^{-2} M). This DA reaction exclusively occurs at the [6,6] conjunct C=C double bond to give the 1 : 1 adduct.[12] The monoaddition generally results in the drop of reactivity to about 1/3 of the parent C_{60} due to the reduced π-conjugation.[13] The progress of the reaction was followed by monitoring the consumption of C_{60} with HPLC according to the previous manner (Fig. S1†).[10,13] The obtained second order rate constants k_2 ($M^{-1}s^{-1}$) are collected in Table 1 along with the Reichardt's solvent polarity parameter $E_T(30)$[9] and the solvent basicity parameter D_π reflecting the electron pair donor (EPD) basicity.[10,14] The kinetic data indicated that C_{60} is 1.3–2.1 times more reactive than C_{70}.[15] In previous work, we have obtained almost the same values of 1.3–2.0 for 1,3-dipolar cycloaddition of C_{60}/C_{70} with various *m*- and *p*-substituted diazodiphenylmethanes.[10] It was also found that a plot of log $k_2(C_{70})$ *vs.* log $k_2(C_{60})$ provided an excellent linear correlation (eqn (1) and Fig. 1). The slope of 1.2 means there is a little more enhanced susceptibility of the C_{70} reaction on the nature of the solvents compared to the C_{60} reaction. This is probably because of the slightly more polar C_{70} transition state as estimated from the somewhat stronger electron-withdrawal of C_{70} ($E_{red} = -0.41$ (*vs* SCE, CH_2Cl_2) *vs.* C_{60} (− 0.44 V)).[16]



Scheme 1 Diels–Alder reaction of C_{60}/C_{70} with 1,3-cyclohexadiene.

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Table 1 Second-order rate constants k_2 for the Diels–Alder reaction of C_{60} and C_{70} with 1,3-cyclohexadiene at 30 °C in various solvents

		$10^5k_2{}^a(M^{-1}s^{-1})$			
	Solvents	C_{60}	C_{70}	$E_T(30)$	$D_\pi{}^b$
1	Benzonitrile	22.6	17.7	41.6	− 0.398
2	Bromobenzene	14.7	9.64	36.6	−1.03
3	*o*-Dichlorobenzene	14.1	9.00	38.0	−1.17
4	Anisole	13.7	8.84	37.1	−0.043
5	Chlorobenzene	13.3	8.26	36.8	−0.903
6	1-Methylnaphthalene	12.8	—	35.3	0.262
7	Benzene	12.1	7.52	34.3	0.000
8	Toluene	10.8	—	33.9	0.394
9	Dichloromethane	10.3	6.43	41.1	−1.30
10	Tetralin	9.74	5.77	33.5	0.650
11	Carbon disulfide	8.95	5.33	32.8	—
12	Tetrachloromethane	8.68	4.82	32.4	—
13	Trichloromethane	7.91	4.80	39.1	−1.56
14	*n*-Hexane	7.77	4.70	31.0	—
15	*p*-Xylene	7.47	4.58	33.1	0.846
16	Mesitylene	5.74	3.37	32.9	1.36

[a] Average of at least two measurements. Error limit is ±2%. [b] The D_π values for *o*-dichlorobenzene, 1-methylnaphthalene, and tetralin were newly obtained according to the previous procedure[14]

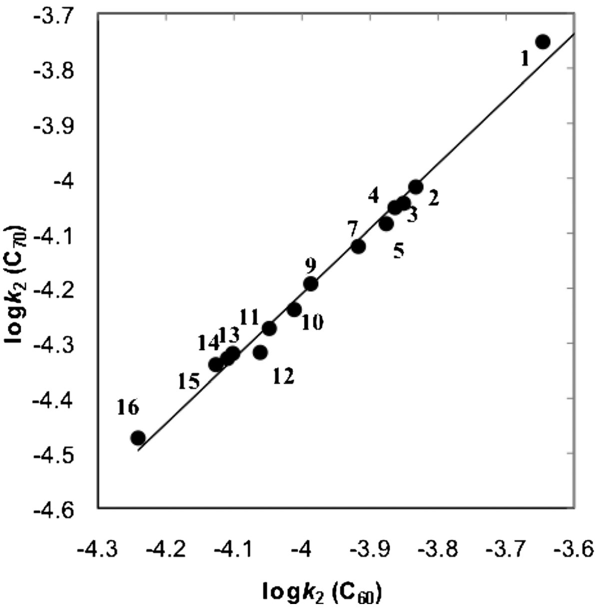

Fig. 1 A plot of log $k_2(C_{70})$ *vs.* log $k_2(C_{60})$ for the Diels–Alder reaction with cyclohexadiene in 14 aprotic solvents. For point numbers, see Table 1.

$$\log k_2\ (C_{70}) = 1.18\log k_2\ (C_{60}) + 0.512\ (R^2 = 0.99,\ n = 14) \tag{1}$$

For the overall kinetic solvent effects, we must consider the solvation of both the initial reactants and the transition state.[9] A survey of Table 1 shows a very small variation of k_2 regardless of a wide range of $E_T(30)$ (31.0–41.6); *i.e.*, $k_{\text{benzonitrile}}/k_{\text{mesitylene}}$ = *ca.* 4 and 6 for C_{60} and C_{70} reactions, respectively. This finding implies that the DA reactions of C_{60}/C_{70} with cyclohexadiene proceed through the less polar transition states.

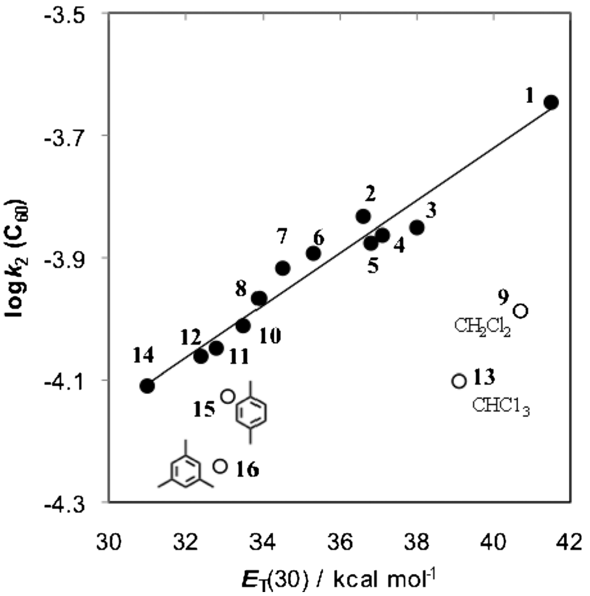

Fig. 2 Plots of log k_2 (C_{60}) *vs* $E_T(30)$ in various solvents. 12 solvents included in the correlation (eqn (2)); 4 outlying solvents (open circle) were excluded from the correlation. For point numbers, see Table 1.

Nevertheless, a plot of log $k_2(C_{60})$ with the solvent polarity parameter $E_T(30)$ gave an excellent linear free energy relationship with very gentle slope ($m = 0.0429$, $R^2 = 0.96$) except for downward deviating four solvents; *p*-xylene, mesitylene, CH_2Cl_2, and $CHCl_3$ (eqn (2) and Fig. 2). The C_{70} reaction also provided a similar plot of log $k_2(C_{70})$ *vs* $E_T(30)$ except the same deviating solvents ($m = 0.0541$, $R^2 = 0.95$, $n = 10$; Fig. S2†). As a consequence of poor solvation, we could take advantage of the present DA reaction as the model reaction in evaluating the delicate specific solute–solvent interaction of the initial-state C_{60} (*vide infra*).

$$\log k_2\ (C_{60}) = 0.0429E_T(30)\ -\ 5.44\ (R^2 = 0.96,\ n = 12) \tag{2}$$

The apparent downward deviation from the regression line may be related to the increase in $\Delta G^{\neq}$ (Gibbs free energy of activation) by about 0.64 and 1.0 kcal mol^{-1} at 30 °C for the typical mesitylene and $CHCl_3$, respectively. The free energy gain of retarding the rate should be ascribed to the specific solvation of the initial-state C_{60}. The typical π-donor solvents, *p*-xylene and mesitylene, do perform the definite charge-transfer type face-to-face π/π interaction with π-acceptor C_{60},[3] bringing about the noticeable rate reduction (*vide infra*). Such an interaction is well recognized in aromatic solvents[17] and also in solvate formation with some aromatic solvents,[7] as well as in the inclusion complexation with various π-conjugated systems.[18] By contrast, however, CH_2Cl_2 and $CHCl_3$ do not form a π/π complex with C_{60}, hence their deviations must be attributable to a quite different type of solute–solvent interaction. As to the specific solvation of these haloalkanes, we will describe this in the later section.

Since the present DA reaction belongs to the normal $\text{HOMO}_{\text{diene}}$–$\text{LUMO}_{\text{fullerene}}$ controlled type, the basic π-donor solvents raise the fullerene LUMO energy due to the π-electron donation and hence decrease the reaction rate.[19] Indeed, the DA reaction of the stronger π-acceptor TCNE with anthracene exhibited a more enhanced rate reduction with increasing solvent π-basicity and gave a good linear free energy relationship between log k_2 and D_π (slope $m = -0.76$, $R^2 = 0.93$, $n = 11$, for some data by extrapolation at 30 °C).[20] The D_π parameter was also successfully applied to the kinetic solvent effects of the typical π-acceptor reactions, eg, 1,3-dipolar cycloadditions of DDM with 2,3-dichloro-5,6-dicyano-4-benzoquinone (DDQ),[21] 2,3-dicyano-4-benzoquinone,[22] fluoranil,[22] as well as C_{60}.[10]

With these considerations in mind we attempted to correlate log $k_2(C_{60})$ with D_π in order to evaluate the π-acceptor ability of fullerenes. Surprisingly, however, a Λ-shaped plot with two solvent groups (*line a* and *b*) was observed with the peak top at the most polar benzonitrile (Fig. 3). The *line a* solvents are characterized by nonhaloarene π-donor solvents and gave a good regression equation with the negative slope (eqn (3), $m = -0.309$). This rate decreasing tendency with increasing D_π may be caused by the stabilization of C_{60} due to the π–π interaction. However, the less basic *line b* solvents including $CHCl_3$ and CH_2Cl_2 as well as all haloarene solvents showed the unexpected rate increasing tendency with increasing D_π (eqn (4), $m = 0.371$).

$$\log k_2\ (C_{60}) = -0.309 D_\pi - 3.84\ (R^2 = 0.93,\ n = 8) \quad (3)$$

$$\log k_2\ (C_{60}) = 0.371 D_\pi - 3.49\ (R^2 = 0.91,\ n = 6) \quad (4)$$

Why do the *line b* solvents exhibit the reverse rate rising tendency with increasing D_π basicity? Before discussing this intriguing phenomenon, it is worthwhile to note that some *line b* solvents such as $CHCl_3$, chloro- and bromobenzenes rather accelerated the rate of the DA reaction of TCNE with anthracene[20] and gave an excellent linear correlation between log k_2 and D_π including several *line a* solvents like benzene and toluene. Therefore, the answer seems to be the switching in the solvation manner of C_{60} from the π–π interaction (*line a*) to the CH/π interaction (*line b*).[8,23] A systematic search in the Cambridge Structural Database disclosed that the CH/π interactions work between the C_{60} convex surface and the haloalkanes such as $CHCl_3$ and CH_2Cl_2 as well as the aromatic compounds.[8] Atwood *et al.* reported these haloalkanes are effective solvents in retrieving guest C_{60} from some inclusion complexes with cyclotriveratrylene and calixarenes probably because of the CH/π interaction with i) host molecules and/or ii) guest C_{60}.[18a,24] Although *line a* aromatic solvents perform the dominant face-to-face π/π interaction with C_{60}, the *line b* haloarene solvents would show edge-to-face type CH/π interaction,[25] accounting for the abnormal lower deviation. To the best of our knowledge, this is the first observation of the solute–solvent CH/π interaction of C_{60} because the present DA reaction undergoes very poor transition-state solvation (Table 1). According to Pearson's hard–soft–acid–base principle,[26] the CH/π interaction occurs between a C–H bond of soft acid and a π-bond of soft base. The present CH/π interaction can be explained in such a way that the soft acidic unoccupied C–H σ*-bond (LUMO+3, +0.07 eV, Fig. S3†)[27] of $CHCl_3$ do not effectively interact with the very lower lying HOMO (−9.41 eV)[27] of the soft π-acid TCNE, but with the 60π-conjugated high lying HOMO (−6.40 eV)[27] of C_{60}. On the other hand, similar calculation for the strong π-donor mesityrene gave a rather high HOMO (−6.42 eV),[27] which could interact with the lower lying LUMO (−3.68 eV) of C_{60} (Fig. 4 a).

It seems likely that C_{60} can perform multi CH/π and π/π interactions on the spherical surface with larger exterior π-orbital lobes, as depicted in Fig. 4 (b) and (c). Thus, the desolvation of the bound solvent molecules is responsible for the rate reduction in the present DA reaction. Although the energy of CH/π interaction of $CHCl_3$ with aromatic hydrocarbons is reported to be as small as 1.5–3 kcal mol^{-1},[28] this weak molecular force plays a vital role in many areas of chemistry and biology.[8c,23a] As such

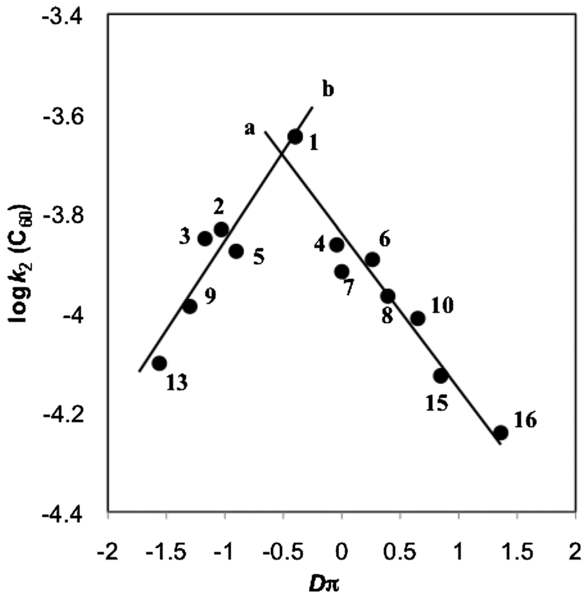

Fig. 3 Plots of log k_2 (C_{60}) *vs* D_π. For point numbers, see Table 1.

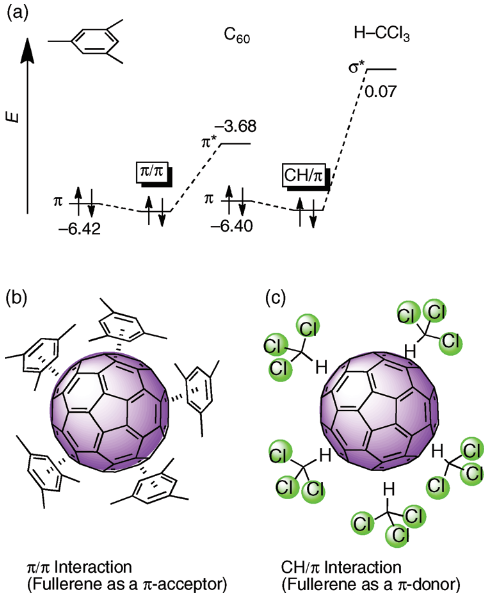

Fig. 4 (a) Orbital interactions of possible solute–solvent interaction between C_{60} and mesitylene/$CHCl_3$; the orbital energy level (eV) was calculated by B3LYP/6-31+G*. Schematic representation of (b) π/π interaction with mesitylene and (c) CH/π interaction with $CHCl_3$; positional geometry and number of solvents are arbitrarily drawn.

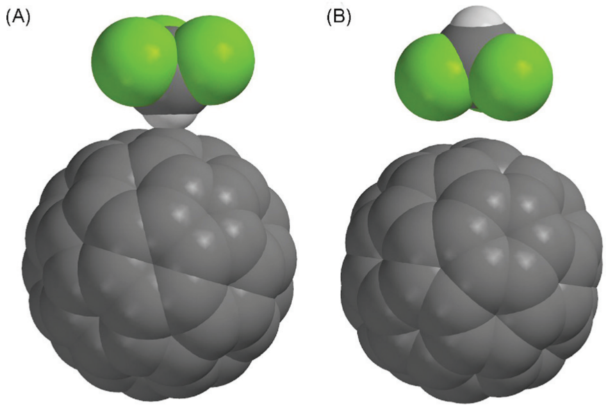

Fig. 5 Bimolecular calculations of C_{60} and trichloromethane by B3LYP/6-31+G*; (A) C–H bond directs to the centre of C_{60}, (B) C–H bond directs to the outside.

CH/π interaction, C–H bond would more favorably orient itself above the pyramidalized sp2 carbon of C_{60} to give maximum overlap between the relevant orbitals. Of interest is that the haloarene solvents are likely to form the well-recognized edge-to-face CH/π interaction in preference to the π/π interaction because the electron-withdrawing halogen substituents will reduce the electron density on aromatic rings and instead enhance the C–H soft acidity.[29]

To assess the CH/π stabilization energy of C_{60}, we resorted to a simplified bimolecular model using a rough DFT calculation (B3LYP/6-31+G*). It was found that the geometry (A) in which the C–H bond of $CHCl_3$ is directed inside to the C_{60} π-face is 0.49 kcal mol^{-1} more stable than the outside-directed geometry (B) in which there is no interaction between C_{60} and $CHCl_3$ (Fig. 5).[30] This value is in reasonable agreement with the above estimated 1.0 kcal mol^{-1} for the $CHCl_3$ deviation from the regression line (Fig. 2). In geometry (A), the C–H hydrogen is in contact with one of the 6,6-conjunct double bonds of C_{60}, where the π-electron cloud is most effectively distributed. The CH–C(C_{60}) carbon atomic distance (D_{ATM}) is 2.86 Å. This value is essentially the same as the mean distance (2.85 Å) of the CH/π interaction of crystalline fullerene compounds in the Cambridge Structural Database.[8a]

In summary, the kinetic solvent effects of the Diels–Alder reaction of C_{60}/C_{70} with 1,3-cyclohexadiene were investigated in 16 aprotic solvents. The correlation of log k_2 with the empirical solvent polarity or the basicity parameter, $E_T(30)$ or D_π, revealed the appreciable CH/π and π/π solute–solvent interactions of initial-state C_{60} thanks to the poor solvation of the transition state. This solute–solvent CH/π interaction is the first example in fullerene chemistry.

Notes and references

1 (*a*) S. R. Wilson, D. I. Schuster, B. Nuber, M. S. Meier, M. Maggini, M. Prato, R. Taylor, *Fullerene Chemistry, Physics and Technology*, John Wiley & Sons Inc. New York, 2000, pp.91–176; (*b*) A. Hirsch, M. Brettreich, *Fullerenes Chemistry and Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005; (*c*) C. Thilgen and F. Diederich, *Chem. Rev.*, 2006, **106**, 5049; (*d*) F. Giacalone and N. Martin, *Chem. Rev.*, 2006, **106**, 5136; (*e*) Y. Matsuo and E. Nakamura, *Chem. Rev.*, 2008, **108**, 3016; (*f*) N. Martín, F. Giacalone. (eds), *Fullerene Polymers*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2009.

2 (*a*) N. Sivaraman, T. G. Srinivasan, P. R. V. Rao and R. Natarajan, *J. Chem. Inf. Model.*, 2001, **41**, 1067; (*b*) Y. Marcus, A. L. Smith, M. V. Korobov, A. L. Mirakyan, N. V. Avramenko and E. B. Stukalin, *J. Phys. Chem. B*, 2001, **105**, 2499; (*c*) J.-C. Huang, *Fluid Phase Equilib.*, 2005, **237**, 186.

3 (*a*) R. Seshadri, C. N. R. Rao, H. Pal, T. Mukherjee and J. P. Mittal, *Chem. Phys. Lett.*, 1993, **205**, 395; (*b*) S. H. Gallagher, R. S. Armstrong, P. A. Lay and C. A. Reed, *Chem. Phys. Lett.*, 1996, **248**, 353; (*c*) M. V. Korobov, A. L. Mirakyan, N. V. Avramenko, G. Olofsson, A. L. Amith and R. S. Ruoff, *J. Phys. Chem. B*, 1999, **103**, 1339; (*d*) K. Datta, M. Banerjee, B. K. Seal and A. K. Mukherjee, *J. Chem. Soc., Perkin Trans. 2*, 2000, 531; (*e*) E. B. Stukalin, M. V. Korobov and N. V. Avramenko, *J. Phys. Chem. B*, 2003, **107**, 9692; (*f*) G. Sarova and M. N. Berberan-Santos, *J. Phys. Chem. B*, 2004, **108**, 17261; (*g*) M. H. Herbst, G. H. M. Dias, J. G. Magalhães, R. B. Tôrres and P. L. O. Volpe, *J. Mol. Liq.*, 2005, **118**, 9; (*h*) I. F. Gun'kin and N. Y. Loginova, *Russ. J. Gen. Chem.*, 2006, **76**, 1911.

4 (*a*) Y. Nagano, T. Tamura and T. Kiyobayashi, *Chem. Phys. Lett.*, 1994, **228**, 125; (*b*) R. Céolin, V. Agafonov, B. Bachet, A. Gonthier-Vassal, H. Szwarc, S. Toscani, G. Keller, C. Fabre and A. Rassat, *Chem. Phys. Lett.*, 1995, **244**, 100; (*c*) M. Jansen and G. Waidmann, *Z. Anorg. Allg. Chem.*, 1995, **621**, 14.

5 (*a*) N. D. Kushch, I. Majchrzak, W. Ciesielski and A. Graja, *Chem. Phys. Lett.*, 1993, **215**, 137; (*b*) R. E. Dinnebier, O. Gunnarsson, H. Brumm, E. Koch, P. W. Stephens, A. Huq and M. Jansen, *Science*, 2002, **296**, 109; (*c*) Q-R. Zheng, G. Su and B. Jin, *Phys. Lett. A*, 2003, **318**, 480.

6 M. F. Meidine, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1534.

7 M. V. Korobov, A. L. Mirakian, N. V. Avramenko, E. F. Valeev, I. S. Neretin, Y. L. Slovokhotov, A. L. Smith, G. Olofsson and R. S. Ruoff, *J. Phys. Chem. B*, 1998, **102**, 3712.

8 (*a*) H. Suezawa, T. Yoshida, S. Ishihara, Y. Umezawa and M. Nishio, *CrystEngComm*, 2003, **5**, 514; (*b*) M. Nishio, *CrystEngComm*, 2004, **6**, 130; (*c*) M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama and H. Suezawa, *CrystEngComm*, 2009, **11**, 1757.

9 (*a*) C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319; (*b*) C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Verlag, 3rd ed., Weinheim, Germany, 2003, Chapter 5, p. 147ff.

10 T. Oshima, H. Kitamura, T. Higashi, K. Kokubo and N. Seike, *J. Org. Chem.*, 2006, **71**, 2995.

11 (*a*) J. B. Briggs and G. P. Miller, *C. R. Chim.*, 2006, **9**, 916; (*b*) S. Osuna, J. Morera, M. Cases, K. Morokuma and M. Solà, *J. Phys. Chem. A*, 2009, **113**, 9721.

12 B. Kräutler and J. Maynollo, *Tetrahedron*, 1996, **52**, 5033 The 1 : 1 adducts of C_{70} were not identified because C_{70} has 4 types of reactive [6,6] bonds leading to several regioisomers in contrast to C_{60} which has only one type of [6,6] bond. See, J. Mestres, M. Duran and M. Solà, *J. Phys. Chem.*, 1996, **100**, 7449.

13 (*a*) N. Ikuma, Y. Susami and T. Oshima, *Org. Biomol. Chem.*, 2010, **8**, 1394; (*b*) N. Ikuma, Y. Susami and T. Oshima, *Eur. J. Org. Chem.*, 2011, 6452.

14 T. Oshima, S. Arikata and T. Nagai, *J. Chem. Res.*, 1981, **(S) 204**, (M) 2518.

15 This rate ratio is considerably smaller than the corresponding value of 7 for the DA reaction of C_{60}/C_{70} with cyclopentadiene at 20 °C in toluene. See: L. S. K. Pang and M. A. Wilson, *J. Phys. Chem.*, 1993, **97**, 6761.

16 D. Dubois, K. M. Kadish, S. Flanagan, R. E. Haufer, L. P. F. Chibante and L. J. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 4364.

17 I. F. Gun'kin and N. Y. Loginova, *Russ. J. Gen. Chem.*, 2009, **79**, 2351.

18 (*a*) J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1994, **116**, 10346; (*b*) J. L. Atwood, M. J. Barnes, M. G. Gardiner and C. L. Raston, *Chem. Commun.*, 1996, 1449; (*c*) J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229; (*d*) T. Suzuki, K. Nakamura and S. Shinkai, *Chem. Lett.*, 1994, 699; (*e*) E. C. Constable, *Angew. Chem.*, 1994, **106**, 2359, (*Angew. Chem., Int. Ed. Engl*, 1994, **33**, 2269); (*f*) T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem.*, 1997, **109**, 288, (*Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 259); (*g*) A. Ikeda, Y. Suzuki, M. Yoshimura and S. Shinkai, *Tetrahedron*, 1998, **54**, 2497; (*h*) T. Kawase and H. Kurata, *Chem. Rev.*, 2006, **106**, 5250; (*i*) K. Tashiro and T. Aida, *Chem. Soc. Rev.*, 2007, **36**, 189; (*j*) T. Iwamoto, Y. Watanabe, T. Sadahiro, T. Haino and S. Yamago, *Angew. Chem.*, 2011, **123**, 8492, (*Angew. Chem., Int. Ed.*, 2011, **50**, 8342).

19 (*a*) J. Sauer and R. Sustmann, *Angew. Chem.*, 1980, **92**, 773, (*Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 779); (*b*) C. Cativiela, J. I. Garcta,

J. A. Mayoral and L. Salvatella, *Chem. Soc. Rev.*, 1996, **25**, 209; (*c*) C. Cativiela, J. I. García, J. Gill, R. M. Martínez, J. A. Mayoral, L. Salvatella, J. S. Urieta, A. M. Mainar and M. H. Abraham, *J. Chem. Soc., Perkin Trans. 2*, 1997, 653.

20 P. Brown and R. C. Cookson, *Tetrahedron*, 1965, **21**, 1977.

21 T. Oshima and T. Nagai, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2039.

22 T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1985, **26**, 4785.

23 (*a*) M. Nishio, M. Hirota, Y. Umezawa, *The CH/Interaction. Evidence, Nature, and Consequence*, Wiley-VCH: New York, 1998; (*b*) S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami and K. Tanabe, *J. Phys. Chem. A*, 2002, **106**, 4423; (*c*) O. Takahashi, Y. Kohno and M. Nishio, *Chem. Rev.*, 2010, **110**, 6049.

24 (*a*) J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston,, *J. Chem. Soc., Chem. Commun.*, 1992, 1349; (*b*) J. L. Atwood, L. J. Barbour, C. L. Raston and I. B. N. Sudria, *Angew. Chem.*, 1998, **110**, 1029, (*Angew. Chem., Int. Ed.*, 1998, **37**, 981); (*c*) J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston and C. A. Sandoval, *Chem.–Eur. J.*, 1999, **5**, 990.

25 (*a*) E. Kim, S. Paliwal and C. S. Wilcox, *J. Am. Chem. Soc.*, 1998, **120**, 11192; (*b*) F. Hof, D. M. Scofield, W. B. Schweizer and F. Diederich, *Angew. Chem.*, 2004, **116**, 5166, (*Angew. Chem., Int. Ed.*, 2004, **43**, 5056); (*c*) I. K. Mati and S. L. Cockroft, *Chem. Soc. Rev.*, 2010, **39**, 4195.

26 (*a*) R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533; (*b*) R. G. Pearson, *J. Chem. Educ.*, 1987, **64**, 561.

27 Calculated values by B3LYP/6-31+G* with SPARTAN'08 software. Full citation of the software is shown in the Supporting Information

28 R. Ehama, M. Tsushima, T. Yuzuri, H. Suezawa, K. Sakakibara and M. Hirota, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 814.

29 (*a*) S. Paliwai, S. Geib and C. S. Wilcox, *J. Am. Chem. Soc.*, 1994, **116**, 4497; (*b*) K. Nakamura and K. N. Houk, *Org. Lett.*, 1999, **1**, 2049.

30 The HOMO level of supramolecule A is −6.48 eV (B3LYP/6-31+G*), slightly lower than that of pristine C_{60} (−6.40 eV), indicating a weak orbital interaction as depicted in Fig. 4a. On the other hand, the HOMO level of B is −6.35 eV, indicating no orbital interaction between C_{60} and $CHCl_3$