Pergamon

Tetrahedron Letters, Vol. 35, No. 25, pp. 4371-4374, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)E0785-V

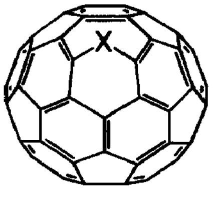
Synthesis and Structure of Nitrene-C_{60} Adduct, C_{60}NPhth (Phth = Phthalimido)

Shin-ya Kuwashima, Masayuki Kubota, Katsuhiko Kushida,[†]
Takayuki Ishida, Mamoru Ohashi, and Takashi Nogami[*]

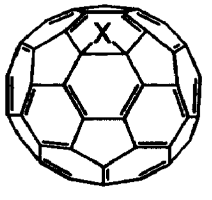
Department of Applied Physics and Chemistry, The University of Electro-Communications,
Chofugaoka, Chofu, Tokyo 182, Japan
[†]Varian Japan Ltd., Sumitomo Shibaura Bldg., 4-16-36 Shibaura, Minato-ku, Tokyo 108, Japan

Abstract: Phthalimidonitrene (:NPhth) generated from H_2NPhth and lead tetraacetate in chlorobenzene was found to add to C_{60}, affording $C_{60}(NPhth)_n$ (n=1-4). The adducts were separated, and the mono-adduct was spectroscopically characterized as an aziridine structure at a 6/6-ring junction. The electron affinity and aziridine inversion are significantly influenced by the substituents on the aziridine nitrogen.

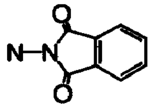
Recently we reported the synthesis, isolation, and characterization of the C_{60} adducts with benzyne, dienes, and dichlorocarbene.[1] The structures of the adducts are attracting much attention in connection with reaction mechanisms. The 1,3-dipolar addition of diazomethane to C_{60} followed by pyrolysis gave fulleroid **1** (an open structure at a 5/6-ring junction),[2] whereas direct addition reactions of carbenes to C_{60} gave methanofullerenes **2** (a closed structure at a 6/6-ring junction).[1c,3] Similar stepwise reaction from C_{60} and alkyl azido reagents afforded open azafulleroids (*e.g.* **3**).[4] We have very recently reported the synthesis and characterization of the first fullerene aziridine **4**.[5] However, there has so far been no report on characterization of adducts obtained by direct addition of nitrenes to fullerenes. The oxidative addition reaction of *N*-aminophthalimide and (*E*)-stilbene giving *trans*-2,3-diphenyl-*N*-phthalimidoaziridine is described in *Organic Syntheses*.[6] The high stereoselectivity suggests that singlet phthalimidonitrene is generated as an intermediate.[7] The nucleophilicity of the nitrene is also pointed out for a resonance contribution of >N-N: ⟷ $>N^+=N^-$.[7] We applied this method to the fullerene chemistry, and obtained the adduct of C_{60} (**5**), the first fullerene hydrazine derivative.



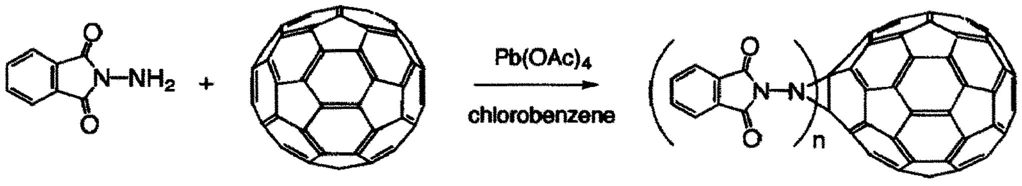
1 X = CH_2
3 NCH_2Ph



2 X = CR_2
4 $NCO_2CH_2CH_3$
5



The following procedure is typical. A mixture of C_{60} (72.5 mg), *N*-aminophthalimide (H_2NPhth, 16.5 mg), lead tetraacetate (95.6 mg, purity 90%), and chlorobenzene (30 mL) was stirred at room temperature for 48 h under argon. The solution turned reddish brown. An aqueous work-up followed by evaporation of the solvent under reduced pressure gave a black residue. It was separated on an HPLC (LC 908, Japan Analytical Industry) by using gel permeation columns (Jaigel 1H+1H) and toluene as an eluent, affording 30.3 mg of $C_{60}NPhth$ (**5**, yield 34%), 14.1 mg of $C_{60}(NPhth)_2$ (14%),[8] 4.3 mg of $C_{60}(NPhth)_3$ (4%),[8] a trace amount of $C_{60}(NPhth)_4$, and 30.2 mg of C_{60} recovered (42%).[9] The intermediate (:NPhth) was proved to be efficiently trapped by C_{60} (>70% based on H_2NPhth). All of the products are dark brown powder (mp. >360 °C). The negative ion FAB MS of the products were measured on a Finnigan Mat. TSQ 700. Samples were ionized by a xenon beam with an energy of 8 kV from a matrix of *m*-nitrobenzyl alcohol. The spectra of the mono-(**5**), di-, tri-, and tetra-adducts showed molecular ion peaks at *m/z* 880, 1040, 1200, and 1361 respectively. The molecular formulae of the reaction products were assigned from these mass numbers. An intense peak at *m/z* 720 of the fragment $C_{60}^{-\cdot}$ was observed for all of the adducts.



5 (n=1,34%)

The structure of monoadduct **5** was spectroscopically determined as follows. The UV/Vis absorption spectrum[10] of **5** was similar to those of the fullerene cyclopropanes[1c,3,11,12] and epoxide,[13] and practically identical with that of aziridine **4**.[5] The IR absorption spectrum[14] showed strong bands due to the imide group together with fullerene bands. The ^1H NMR exhibited a typical coupling pattern of a symmetrical *o*-phenylene group.[15] In the FAB MS/MS measurement of $\mathbf{5}^{-\cdot}$ as a precursor ion (collision gas: Ar, $1x10^{-3}$ Torr, acceleration energy: 40 eV), the fragments $C_{60}N^-$ and $Phth^-$ were clearly observed at *m/z* 734 and 146 respectively, which are given from a possible N-N bond scission.

The 100 MHz ^{13}C NMR spectrum of **5** exhibited 21 signals in C_6D_6 at 75 °C.[16] The signals at δ 163.9 and 81.9 are ascribable to the carbonyl and quaternary bridgehead carbons respectively. A short pulse interval ($\leq$ 3 sec) decreased the relative signal intensity at δ 81.9, indicating that this signal can be ascribed to the carbons bonded to nitrogen. All of the other signals in the aromatic region can be assigned to the *o*-phenylene carbons (3 signals) and fullerene carbons (16 signals in δ 140-146, Fig. 1a). These findings indicate the following structural informations. The C_{60} moiety has a C_{2v} symmetry showing 17 resonances; the addition occurred at a 6/6-ring junction. The chemical shift of the bridgehead carbons is consistent with a closed aziridine structure,[5] and not with an open azafulleroid.[4] The resonances of the bridgehead carbons in the closed cyclopropanes[1c,3,11,12] and epoxide[13] were reported to appear at δ 77-80 and 90.2 respectively, which are close to those of the aziridines with slight shifts mainly due to the electronegativities of the different atoms attached.

The inversion of the aziridine nitrogen seems nearly free at 75 °C in the time scale of our NMR measurements. However, several ^{13}C signals were broadened at 75 °C, and 3 signals were undetectable at 25

°C (Fig. 1b).[17] The bridgehead signal remained sharp. Therefore, this behavior has no relation to the valence tautomerism between the closed and open isomers. This can be interpreted that the signals arising from a C_s structure due to a pyramid of the aziridine nitrogen coalesce at about 25 °C and that the time-averaged C_{2v} structure was observed at 75 °C owing to a rapid inversion. In general, conjugatively electron-withdrawing substituents on the nitrogen lower the energy barrier of the inversion, while amino, methoxy, and halogeno groups raise the barrier.[18] It holds for the cases of the fullerene derivatives; a carbonylated aziridine, $C_{60}NCO_2Et$, shows sharp ^{13}C resonances due to a rapid inversion at 25 °C,[5] and an *N*-aminoaziridine derivative **5** shows the relatively slow inversion under the same conditions. The inductive and/or steric effects of the C_{60} moiety also decreases the inversion barrier of **5**; this is compared with the facts that the inversions of 1-aminoaziridine[19] and methyl 1-phthalimidoaziridine-2-carboxylate[7] are reported to be slow up to 150 and 130 °C, respectively, in the NMR time scale.

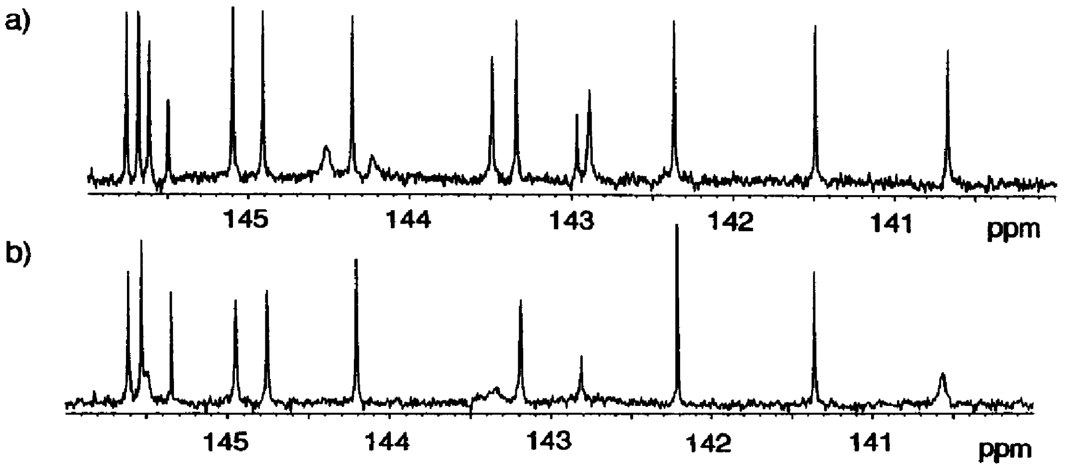


Fig. 1. Fulleroid region of ^{13}C NMR spectrum of **5** (100 MHz, C_6D_6). a) Measured at 75 °C with some signals motionally broadened. b) Measured at 25 °C with 3 signals undetectable.

The cyclic voltammetry[20] of **5** revealed the presence of irreversible process and weaker electron-accepting properties than those of C_{60}. The first peak positions of the reduction potentials are -1.22 and -0.97 V for **5** and C_{60}, respectively, against the Ag/Ag$^+$ reference electrode, suggesting that the C_{58} conjugation has a higher energy level of LUMO than the C_{60} conjugation does. The shift of **5** (-0.25 V) relative to C_{60} is somewhat larger than that of **4**.[5] This finding can be accounted for in terms of substituent effects. The electron-donating amino group on the aziridine nitrogen in **5** decreases the electron affinity of the C_{60} moiety, unlike the case of the electron-withdrawing carbonyl group in **4**. It has recently been reported that the epoxide $C_{60}O$ is a stronger acceptor than C_{60}.[21] The electronegativities of O and N atoms explain the order of the electron accepting properties of the derivatives: epoxide > C_{60} ≥ aziridines.

The 1,3-dipolar addition of diazo compounds to C_{60} and loss of nitrogen gave the fulleroids.[2] The methanofullerenes are obtained by thermal rearrangement of the bridge in the fulleroid once formed.[12,22] On the other hand, the closed isomer was selectively obtained in the preparation of **2** (R=Cl,[1c] OMe[3b]), where a direct carbene attack occurs at a reactive 6/6-ring junction. In the chemistry of the nitrogen-bridged fullerene, the present synthesis can be compared with that of the reaction of C_{60} with alkyl azido reagents giving only open azafulleroids.[4,23] The formation of **5** provides an example for a direct and selective attack of nitrene to C_{60} at a 6/6-ring junction. This nitrene route is complementary to the azido route in preparation of two types of the nitrogen-bridged fullerene derivatives, azafulleroids and iminofullerenes.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Carbon Clusters" (No. 05233213), from the Ministry of Education, Science and Culture, Japan.

References and Notes

1. a) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *Chem. Lett.* **1992**, 2333-2334; b) *idem*, *J. Chem. Soc., Chem. Commun.* **1993**, 1296-1298; c) *idem*, *Tetrahedron Lett.* **1993**, 6911-6912.
2. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301-7302.
3. a) Vasella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diederich, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1388-1390; b) Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 2454-2464.
4. Prato, M.; Li, Q. C.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 1148-1150.
5. Ishida, T.; Tanaka, K.; Nogami, T. *Chem. Lett.* **1994**, 561-562.
6. Müller, K.; Joos, R.; Felix, D.; Schreiber, J.; Wintner, C.; Eschenmoser, A. *Org. Synth.* **1988**, *VI*, 56-61.
7. Anderson, D. J.; Gilchrist, T. L.; Horwell, D. C.; Rees, C. W. *J. Chem. Soc. (C)* **1970**, 576-582.
8. The yields were calculated as a mixture of possible isomers. The structure of **5** was determined as described in the text, but those of di-, tri-, and tetra-adducts were tentatively drawn as in the scheme.
9. Retention times: $C_{60}(NPhth)_4$, 59 min; $C_{60}(NPhth)_3$, 65 min; $C_{60}(NPhth)_2$, 74 min; $C_{60}NPhth$, 81 min; C_{60}, 102 min, eluted at a rate of 3.5 mL min^{-1}.
10. UV/Vis (hexane) λ_{max} 215, 252, 319, 423, 493, 680(sh) nm.
11. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186-1188.
12. Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231-1250.
13. K. M. Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, III, A. B.; McCauley, Jr., J. P.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103-1105; Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351-353.
14. IR (KBr disk) 1720, 1365, 1350, 1260, 1130, 1080, 980, 890, 800, 720, 700, 520, 510 cm^{-1}.
15. ^1H NMR (270 MHz, 25 °C, C_6D_6) δ 7.42-7.37 (m, 2H), 6.85-6.80 (m, 2H).
16. $^{13}C\{^1H\}$ NMR (100 MHz, 75 °C, C_6D_6, pulse interval: 10 sec, accumulation: 3 days) δ 163.92 (2, C=O), 145.76 (4), 145.68 (4), 145.61 (4), 145.50 (2), 145.10 (4), 144.91 (4), 144.52 (4), 144.36 (4), 144.23 (2), 143.49 (4), 143.34 (4), 142.97 (2), 142.89 (4), 142.37 (4), 141.49 (4), 140.67 (4), 134.21 (2, *o*-phenylene CH), 130.97 (2, *o*-phenylene C), 123.58 (2, *o*-phenylene CH), 81.89 (2, bridgehead). The carbon abundances shown in parentheses were determined by relative signal integrals.
17. The coalescence of each signal depends on the ratio of the separation of two interchanging signals to the inversion rate. This finding may provide a clue to the signal assignment.
18. Gilchrist, T. L. *Heterocyclic Chemistry*; Pitman Publishing Ltd.: London, 1985; pp. 34-37.
19. Brois, S. J. *Tetrahedron Lett.* **1968**, 5997-6000.
20. The cyclic voltammetry was measured in *o*-dichlorobenzene using 0.1 M $Bu_4N^+ClO_4^-$ as a supporting electrolyte; Pt working and counter electrodes; Ag/Ag$^+$ reference electrode; scan rate, 100 mV/s.
21. Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359-1363.
22. Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479-8480.
23. The synthesis of fullerene aziridines from azido reagents seems to be restricted by a substituent on the nitrogen.[5]

(*Received in Japan* 5 *February* 1994; *accepted* 13 *April* 1994)